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Bengal.

MODERN BLEACHING AGENTS AND DETERGENTS

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BY

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AUTHOR'S PREFACE.

THE present work on modern bleaching agents and detergents falls into two divisions.

In the first a review of the old and more recent bleaching agents and methods is succeeded by a detailed account of those of modern origin. Considerable space has been devoted to a description of the properties of the various new bleaching agents; and in view of the predominantly chemical character of the book, suitable consideration has been bestowed on chemical processes.

In connection with electrical bleaching an endeavour has been made to furnish a succinct account of the present state of the industry.

The second division commences with a general introduction, followed by a few particulars respecting the behaviour of various textile materials under the action of chemicals, thus affording a general idea of the methods by which detergents should be applied. Next follows a description of the chief modern detergents, and of the various methods applicable to the elimination of stains. Due consideration has been given to the behaviour of hydrogen peroxide and oxygenol towards coloured fabrics. In addition to the detergents properly so-called, the modern laundry preparations have received attention, since these cleansing agents may frequently be employed in connection with the same purpose.

MAX BOTTLER.

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CHAPTER I.

OLD AND NEW BLEACHING METHODS AND BLEACHING AGENTS.

Bleaching Agents for Wool.—The proper bleaching agents for wool are: sulphur dioxide or sulphurous anhydride (SO_2), sodium bisulphite or acid sulphite ($NaHSO_4$), hydrosulphurous acid ($H_2S_2O_4$), hydrogen peroxide (H_2O_2), sodium peroxide (Na_2O_2) and potassium permanganate ($KMnO_4$).

The object of bleaching sheep's wool is to change its yellowish tinge to a pure white; and the expression "bleaching" is applied only in its restricted sense in the case of wool and silk, namely, to the operation performed with the object of destroying the colouring matter in the fibre.

Of the bleaching agents mentioned above, gaseous sulphurous acid (sulphur dioxide) has long been used for bleaching wool, the others being modern innovations. In one of the newer processes the yellow natural colour of the wool is permanently removed by means of hydrosulphurous acid; whilst Thierry Mieg & Co. have devised a method of decolorising woollen goods with bisulphite more quickly, cheaply and completely than hitherto practicable.

There are now also several established processes for bleaching wool with hydrogen peroxide. In accordance with the importance of the subject we shall deal thoroughly, in a subsequent chapter, with the bleaching of wool, both as loose fibre, yarns and piece-goods, with sodium peroxide.

Bleaching with Permanganate.—Another agent also employed for wool bleaching is potassium permanganate, on account of its oxidising properties; and when this substance is used the addition of a little magnesium sulphate to the bath must not be forgotten in order to protect the animal fibre (wool or silk) from injury by the caustic alkali liberated by the decomposition of the permanganate. Since this bleaching agent is used for all kinds of textile fibres, whether of animal or vegetable origin, it may not be out of place to elucidate, by means of chemical equations, the processes involved when suitably prepared fibres are bleached with potassium permanganate solution. The first reaction is expressed by:—

$$\underset{\text{Potassium permanganate}}{2KMnO_4} + \underset{\text{Water}}{3H_2O} = \underset{\text{Caustic potash}}{2KOH} + \underset{\text{Manganese perhydroxide}}{2MnO_2 . H_2O} + \underset{\text{Oxygen}}{3O}$$

manganese dioxide being precipitated on the fibre, from which it can be removed by treatment with dilute hydrochloric acid, sulphuric acid, sulphur dioxide or hydrogen dioxide, in accordance with the equations:—

$$(\alpha)\ \underset{\text{Manganese dioxide}}{MnO_2} + \underset{\text{Sulphuric acid}}{H_2SO_4} = \underset{\text{Manganous sulphate}}{MnSO_4} + \underset{\text{Water}}{H_2O} + \underset{\text{Oxygen}}{O};$$

$$(\beta)\ \underset{\text{Manganese dioxide}}{MnO_2} + \underset{\text{Sulphur dioxide}}{SO_2} + \underset{\text{Water}}{H_2O} = \underset{\text{Manganous sulphate}}{MnSO_4} + \underset{\text{Water}}{H_2O};$$

$$(\gamma)\ \underset{\text{Manganese dioxide}}{MnO_2} + \underset{\text{Hydrogen peroxide}}{H_2O_2} + \underset{\text{Hydrochloric acid}}{2HCl} = \underset{\text{Manganous chloride}}{MnCl_2} + \underset{\text{Water}}{2H_2O} + \underset{\text{Oxygen}}{O_2}.$$

The neutralisation of the caustic alkali by means of the magnesium sulphate is effected as follows:—

$$\underset{\text{Caustic potash}}{2KOH} + \underset{\text{Magnesium sulphate}}{MgSO_4} = \underset{\text{Magnesium hydroxide}}{Mg(OH)_2} + \underset{\text{Potassium sulphate}}{K_2SO_4}.$$

Perborates.—The perborates are mentioned more especially because by their aid it is possible to obtain pure solutions of hydrogen peroxide suitable for bleaching fine fabrics.

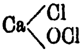
Acid Sodium Percarbonate.—E. Merck of Darmstadt patented a method of making acid sodium percarbonate, which substance is used for medicinal and technical purposes, and more particularly as a disinfectant and for the production of hydrogen peroxide.

Bleaching Agents for Silk.—The ordinary bleaching agent for silk is sulphur dioxide, though use is also made, for this purpose, of sodium bisulphite, potassium permanganate, hydrogen peroxide, sodium peroxide and barium peroxide (BaO_2). In spite of its high price hydrogen peroxide plays an important part in the bleaching of silk, being preferable to any other bleaching agent because it does not corrode this or any other animal fibre. In comparison with gaseous sulphur dioxide it presents the additional advantage of giving a permanent bleach.

Mention should also be made of a new process for bleaching silk, in which the hitherto indispensable preliminary operation of scouring the silk is rendered superfluous by adding glycerine (or alcohol, aldehyde or ketone) to the bleaching solution of hydrogen peroxide. It is also worthy of note that the old practice of bluing the animal fibres (wool or silk) after bleaching is now effected before that operation.

Sodium peroxide and barium peroxide are chiefly used for bleaching tussah silk. In the case of permanganate the procedure is the same as for wool.

Bleaching Powder and Alkali Hypochlorites.—The most important bleaching agents for vegetable fibres are bleaching powder ("chloride of lime") and sodium hypochlorite or the corresponding potassium salt.

Bleaching powder,  $\mathrm{Ca}\left\langle\begin{matrix}\mathrm{Cl}\\ \mathrm{OCl}\end{matrix}\right.$ [$Ca(OCl)_2 + CaCl_2$], is a double salt of calcium hypochlorite and calcium chloride. Of late a solid stable form of calcium hypochlorite has been put on the *market; and this new product contains 80-90 per cent. of* active chlorine, as compared with the 34-36 per cent. present in ordinary commercial bleaching powder, only exceptionally fine grades of which yield as much as 42-46 per cent. of active chlorine.

Sodium hypochlorite (NaOCl) and potassium hypochlorite (KOCl), the bleaching action of which is increased by additions of acid, are usually employed along with hydrochloric acid, though of late this is frequently replaced by acetic acid and even formic acid.

In cleaning and bleaching cotton the fibre is first put through the "bowking" process consisting of a treatment with alkaline substances (mostly lime and hard resin soaps) and is then bleached with bleaching powder, this operation being succeeded by "souring" with sulphuric acid.

The Thies-Herzig Bleaching Process.—Latterly the usual bowking process has been superseded by boiling the cotton with caustic soda alone. In this process (invented by Thies and Herzig) the fibre or fabric is treated in a vacuum pan, and the material must also be quite free from contained air. The actual bleaching is mostly performed with sodium hypochlorite, the solution, however, being only one-third the usual strength. Souring is performed in a bath containing 10 per cent. of sulphuric acid and ½ per cent. of hydrofluoric acid.

The cotton or other textile fibre is first steeped in a ½ per cent. solution of caustic soda, at a temperature of 122° F., and is next washed in water containing 5 per cent. of magnesium chloride. This precipitates sparingly soluble magnesia on the fibre, and the latter suffers no injury, it having been found that fibres that have been impregnated with magnesia or other alkaline earths are neither mercerised nor rotted by subsequent boiling with strong caustic soda. The material is now transferred to the bowking kier, and subjected to the action of hot steam for two to three hours, after which a boiling solution of strong caustic soda, containing *a little resin, is poured in. After treatment with this solution* for about three hours the material is washed with boiling water, followed by the aforesaid bleaching with sodium hypochlorite (or bleaching powder), and then by souring, the material being finally washed.

In bleaching cotton with caustic soda (without magnesium chloride) a very dilute solution (2·5° Bé.) of the alkali is used. The material is soured with hydrochloric acid (½° Bé.); and the actual bleaching is effected by a solution (0·3° Bé.) of bleaching powder, this treatment being followed by souring with hydrochloric acid (½° Bé.). The caustic soda is used in a very dilute form, since a stronger solution would mercerise and also weaken the fibre.

Thompson's Improved Bleaching Process.—It may be mentioned that, about twenty years ago, J. Thompson reintroduced a method which had been patented by F. Didot more than fifty years previously, and consisting in the employment of carbon dioxide for bleaching paper stock, textiles and other materials. In consequence of the construction of improved apparatus this method was afterwards enabled to find practical application, the material, impregnated with a solution of bleaching powder, being treated with gaseous carbon dioxide. The chemical reactions may be expressed by the following equations:—

(α) $Ca(OCl)_2 + CaCl_2 + CO_2 + H_2O = CaCO_3 + CaCl_2 + 2HOCl$;

(β) $2HOCl = 2HCl + O_2$;

(γ) $CaCO_3 + 2HCl = CaCl_2 + CO_2 + H_2O$.

The decomposition of the bleaching powder proceeds in the same manner as under the influence of atmospheric carbon dioxide. Since the hydrochloric acid produced by the decomposition of the hypochlorous acid (equation β), liberates a further quantity of carbon dioxide from the calcium carbonate this dioxide being then in a position to react on fresh quantities of the bleaching powder, the rapidity of the process depends on the amount of carbon dioxide employed. This, in turn, must be regulated in accordance with the quality of the material under treatment, to prevent injury to the fibre from an excessively rapid liberation of hypochlorous acid.

Bleaching Linen.—It is well known that this material can be bleached in the same way as cotton. Owing, however, to the higher percentage of impurities in flax fibre than in raw cotton, and the fact that these substances must be eliminated before the actual bleaching takes place, the operation is a more difficult one.

In the case of linen the chemical reagents must be used more frequently and in a more dilute condition than for cotton, the flax fibres being more sensitive to their action.

By treating the linen alternately with weak solutions of bleaching powder and alkaline baths, the brown pectin bodies in the fibre are gradually transformed into a condition in which they are soluble in alkaline liquids. Their removal is also facilitated by the operation of "grassing" or suspending the linen on frames, on account of the bleaching effect of ozone and hydrogen peroxide.

Cotton and linen may also be bleached with hydrogen peroxide; and a combined method of bleaching fine cotton yarns with hydrogen peroxide and bleaching soda has recently been introduced, which method gives a beautiful white product.

In the case of linen fabrics, grass bleaching can now be replaced by treatment with hydrogen superoxide, but the method is still very complicated and expensive.

Bleaching with Ozone.—Attempts have recently been made to prepare bleaching ozone on a large scale, by the electrical ozonisation of air, in order to replace grass bleaching. The ozonising process is applied more especially to linen yarns, and latterly to raw cotton as well.

Saget's Bleaching Process.—This method, which is applied to raw cotton, employs sodium bisulphite, with or without Turkey-red oil, and is said to yield good results.

Bleaching Straw and Leather.—Bisulphite may also be used for bleaching straw and leather, by new methods specially devised for these purposes.

Discharging Colours.—The process of discharging colours on textile fabrics by means of hydrosulphurous acid, being merely one of bleaching by reduction, will also be dealt with.

Bleaching Jute and other Vegetable Fibres.—Fine jute yarns are not infrequently bleached with permanganate, a new process for using this agent furnishing an almost pure white product. According to another new process, introduced by Martin, the jute is boiled in an autoclave with a mixture of soda, oil of turpentine and carbon disulphide, this preliminary operation being stated to reduce the consumption of the actual bleaching agent by one-half.

Suitable methods have also been devised for bleaching different vegetable fibres (varieties of hemp, Manila hemp, Sisal, Mexican fibre, New Zealand flax) with hydrogen peroxide.

Bleaching Various Substances.—The permanganate method, in combination with a treatment with sodium hyposulphite, has been found to answer in the case of straw; and permanganate is also used in bleaching ivory. Hydrogen peroxide is used in certain new methods for bleaching straw, wood, feathers, hair, sponges, leather, ivory and similar articles.

Electrical Bleaching Processes.—Electricity has recently been called in aid for the bleaching of textile fibres (cotton in all forms, hemp, paper stock, cellulose, etc.), the continuous current being used.

In the electrical bleaching methods now employed the assistance of electricity is indirect, inasmuch as the current only comes in contact with the bleaching liquor. The sole difference between the various methods consists in the construction of the apparatus in which the bleaching liquor is produced by the aid of electricity.

In these electrical processes a solution of common salt is subjected to the action of the current and is then used as bleaching liquor. The effect of the passage of the current is to electrolyse the sodium chloride, chlorine being formed on the one hand, and sodium (or rather caustic soda and hydrogen) on the other. The chlorine dissolves in the aqueous brine and is combined by the caustic soda.

When chlorine is allowed to act on caustic soda lye in the cold a mixture of sodium hypochlorite and sodium chloride is formed. The same occurs during electrolysis; and as it is known that the efficiency of a bleaching liquor depends on the amount of sodium hypochlorite present, the chief point aimed at in electric bleaching is to produce a powerful liquor.

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CHAPTER II.

SODIUM PEROXIDE.

PROPERTIES.—Commercial sodium peroxide, Na_2O_2, is a white to yellowish white powder, deliquescent in the air, and absorbing carbon dioxide with liberation of oxygen. When dissolved in ice water sodium peroxide is converted into caustic soda, heat being generated and hydrogen peroxide formed, the chemical reaction occurring under these conditions being expressed by the equation :—

$$\underset{\substack{\text{Sodium}\\\text{peroxide}}}{Na_2O} + \underset{\text{Water}}{2H_2O} = \underset{\substack{\text{Sodium}\\\text{hydroxide}}}{2NaOH} + \underset{\substack{\text{Hydrogen}\\\text{peroxide}}}{H_2O_2}.$$

The disengagement of oxygen by the hydrogen peroxide under the influence of heat proceeds in accordance with the equation :—

$$\underset{\substack{\text{Hydrogen}\\\text{peroxide}}}{H_2O_2} = \underset{\text{Water}}{H_2O} + \underset{\text{Oxygen}}{O}$$

that is to say, the hydrogen peroxide formed is split up into water and oxygen. Sodium peroxide liberates 20 per cent. of oxygen, whilst hydrogen peroxide (12 per cent. by volume) furnishes 1½ per cent. of oxygen. Kassner has shown that the liberated oxygen also contains ozone.

Dissolving Sodium Peroxide.—At a sufficiently low temperature, sodium peroxide dissolves in water containing acids, hydrogen peroxide and the corresponding sodium salts being formed. In most bleaching processes (wool, silk, etc.) the sodium peroxide must be dissolved in acidified water, in order to neutralise the caustic soda, which would otherwise corrode the fibre. If sulphuric acid be used for this purpose, the neutralisation proceeds in accordance with the equation:—

$$\begin{array}{ccccccc} 2NaOH & + & H_2SO_4 & = & Na_2SO_4 & + & 2H_2O \\ \text{Sodium} & & \text{Sulphuric} & & \text{Sodium} & & \text{Water} \\ \text{hydroxide} & & \text{acid} & & \text{sulphate} & & \end{array}$$

the solution then containing sodium sulphate, which has no weakening influence on the fibre. Pure water alone may be used for dissolving sodium peroxide, and the acid used for neutralising must also be pure, because in the case of impure water a certain amount of oxygen would be wasted in the oxidation of the impurities. The water for making the bleaching liquor should also be as cool as possible, this being a condition essential to the preparation of a solution containing caustic soda and hydrogen peroxide at the same time.

Warm water causes the liberation of oxygen from the peroxide; and hence, during warm weather, the water should be allowed to run out of the pipe some little time before use. A considerable rise in temperature occurs during the dissolving of sodium peroxide.

Preparing the Bleaching Liquor.—This is usually performed by sprinkling the sodium peroxide, from a kind of dredger, into the acidified water, in small quantities at a time, care being taken to keep the water in motion by means of stirrers. Among other disadvantages, the addition of larger quantities of peroxide to the water at any one time is attended with a considerable waste of oxygen. Sodium peroxide is neither combustible nor liable to spontaneous ignition.

By itself, sodium peroxide cannot be exploded by percussion or shock, or even by the heat of the blowpipe flame, though on account of its powerful oxidising action on most organic substances it is capable of igniting cotton, wool, straw, etc., especially in presence of moisture or water. In adding sodium peroxide to the bath, care must be taken to see that none of the powder is spilled, or, in the case of a bleaching 'kier, dropped between the false bottom or sides and the lead coil. The powder must be taken out of the drum or tin by means of a clean metal scoop, which must be perfectly dry, to prevent any decomposition of the peroxide. For the same reason the drum, etc., must be tightly closed after any of the powder has been taken out.

Jaubert's Compressed Sodium Peroxide.—This article forms a dense, hard mass, far less liable to become decomposed by water and heat than the ordinary powder form. No risk of explosion is incurred by bringing this compressed preparation into contact with readily inflammable substances; and when placed in water it does not give rise to the usual brisk effervescence, but only to a temporary gradual liberation of oxygen, this soon ceasing on account of the formation of a film of sparingly soluble perhydroxide ($Na_2O_2 + 8H_2O$). Jaubert has also pressed the powdered peroxide into a solid mass with bisulphate or a solid organic acid, which preparation, on being dissolved in water, furnishes a neutral, faintly acid or faintly alkaline solution, according to the ratio between the peroxide and the acid.

Employment of Sodium Peroxide in Bleaching.—Sodium peroxide is adapted for bleaching wool (loose wool, yarn or fabric), mixed fabrics (half-wool and half-silk), silk (chappe, bourette, tussah), hair, straw, ivory, etc., a very pure and permanent white being obtained, in contrast to the merely temporary bleaching furnished by sulphur dioxide, especially on wool.

Owing to its considerably higher price than bleaching powder (which is also very efficient on that fibre), sodium peroxide is of less importance in the bleaching of cotton, though it is used for half-woollen goods. With these latter fabrics sulphur bleaching is attended by certain difficulties, the cotton being more or less corroded by the sulphurous acid, in consequence of which the addition of alkalis is necessary. These, however, are inadmissible on account of their corrosive action on the wool; whereas sodium peroxide does not injure either kind of fibre, and can therefore be used for bleaching the mixed fabric. In addition to the foregoing textiles sodium peroxide is suitable for bleaching straw, felt, wood, horn, Malacca cane, bones, ivory, bristles, sponges, wax, fats and oils.

Cleaning the Materials to be Bleached.—All the substances to be treated must first be thoroughly cleaned by means of soap or other detergents.

In the case of wool and half-wool it should be noted that unless completely freed from fat the material will not bleach. The best detergent in this case is a solution of ammonia, this alkali making the wool bright and preserving its natural softness. Ammonia, being volatile, there is no risk of its remaining in the wool after the cleansing process. Potash or potash (potassium carbonate) soap may also be used for cleansing wool, the natural softness of which is retained under this treatment, whereas sodium carbonate makes the fibre hard. An excess of alkali should be avoided, especially for fine wool, since it makes the wool yellow, which tinge cannot afterwards be eliminated by the sodium peroxide bleaching process.

For yarns (wool, worsted, merino) and piece-goods the use of ½-1 per cent. of soft soap (Marseilles soap) is recommended along with a little ammonia, whilst for the second washing the water should contain a little ammonia and about ½ per cent. of Turkey-red oil.

For carpet yarns or yarns of low quality about 1-2 per cent. of sodium carbonate, with a little soap and about ½ per cent. of Turkey-red oil, seems applicable, it being desirable to free these from fat as cheaply as possible before bleaching.

Since metals and metallic salts exert a catalytic action on the bleaching liquor, and therefore cause the liberation of oxygen to proceed too rapidly, the bleaching liquor should always be prepared in a perfectly clean and well-bleached wooden vat, an enamelled pan being used when the quantity is small. Where direct steam is used for warming the liquor—as in small works or trial bleachings—lead or earthenware pipes alone are suitable, iron pipes being debarred on account of their tendency to rust.

Testing the Bleaching Liquor.—Before entering the goods to be bleached the liquor must be tested with litmus paper. If the liquor turns red litmus paper blue the bath is alkaline, an acid liquor turning blue litmus red; whilst if no colour-change is produced on either blue or red litmus the liquor is neutral. A neutral or acid liquor must be rendered alkaline.

The arrangement of a cheap vat, which is easily put together, is shown in Fig. 1.

Bleaching Kier.—The wooden kier A is provided with a leaden steam pipe C along the one side, steam being admitted to this pipe through an iron pipe H, and a tap connection being provided at F. The waste steam pipe I is fitted with a safety valve, to prevent the bursting of the pipe in the event of omission to open the waste tap G when steam is admitted at F. A wooden partition D, with holes about 1 inch in diameter, is placed between the steam pipe and the goods in the kier, and is held in place by wooden strips E, fastened by pegs. The goods are held down in the liquor by a wooden frame D, kept in place by wooden blocks J. In order that the process may be worked economically it is essential that no other metal than lead should come in contact with the liquor. A draw-off tap or spigot K is placed in a suitable position at the bottom of the kier, to enable the liquor to be run off completely as soon as necessary.

This kier is suitable for the treatment of various materials: loose fibre, yarns and piece-goods. In the latter case it is fitted with a reel, to enable the goods to be drawn through and out of the kier. Loose wool and lightly twisted yarns should not be handled any more than is necessary during cleaning and bleaching, as otherwise they are liable to felt.

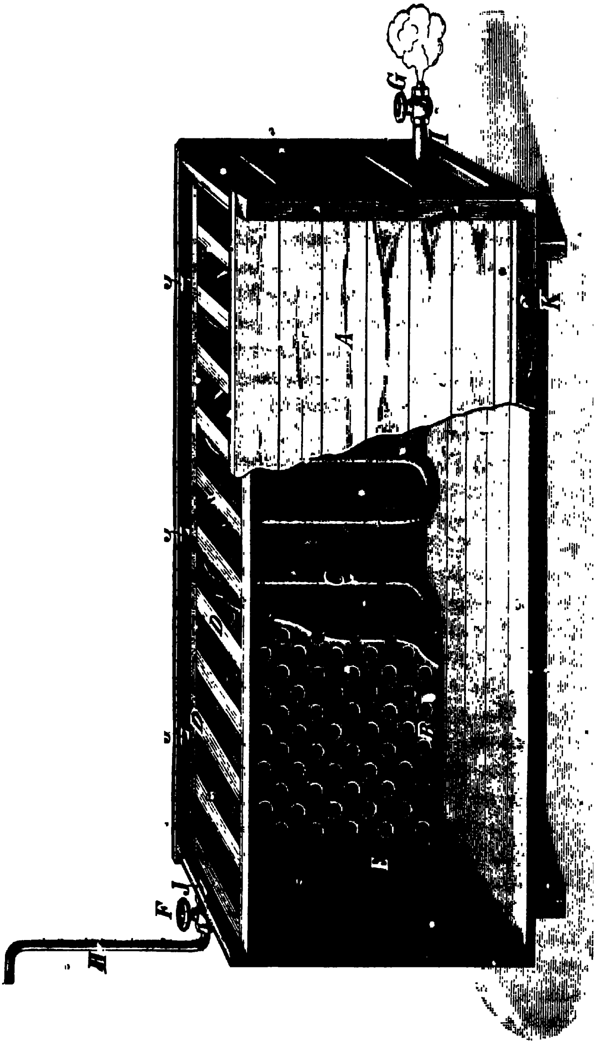

Fig. 1.—Bleaching Kier.

In some cases it is advisable to arrange the heating coil at the bottom instead of at the top, the wooden partition being then mounted as a false bottom.

When the kier is ready for use, with the partition and frame D, these fittings, together with the sticks needed for working the goods in the liquor, are put in the kier and boiled thoroughly in a solution of sodium carbonate, followed by rinsing with water, the kier and fittings being then bleached with a $\frac{1}{2}$ per cent. solution of sodium peroxide, containing 0 675 per cent. of commercial sulphuric acid (66° Bé.). Enough of this solution should be used to fill the kier to above the level of the frame D, the object being to remove any organic impurities and colouring matters present in the wood, and produce the conditions requisite for successful bleaching. Steam is admitted, not forgetting to open the waste steam tap G, the temperature being raised to 140° F., and the whole then left over-night.

Next morning the contents are raised to boiling point, whereupon the kier is emptied, and finally washed out with clean water, which done the kier is ready for use.

As much material—fabric, wool, hanks of yarn, etc.—as the liquor can soak through properly is placed in the kier, bearing in mind that, if packed too tightly, the oxygen liberated from the liquor will be unable to gain access to all parts of the material.

Charging the Kier with Bleaching Liquor.—Particular care is necessary in adding the sodium peroxide to the water and sulphuric (or acetic) acid forming the bath. The powder is sprinkled in in small quantities, preferably with a dredger, whilst a second operative keeps the liquor well stirred with a paddle or stick, so as to enable the peroxide to dissolve at once, since undissolved particles will corrode the fibre. The Natrium Company has put on the market a handy sprinkler, which can be suspended over the kier and ensures proper distribution of the peroxide.

Bleaching Woollen and Half-wool Goods.—Wool, wool felt, half-wool (cotton and wool) fabrics, woollen yarn and woollen plush can be bleached in the following manner:—

Before bleaching, the goods are thoroughly cleansed of all impurities by means of soap and ammonia or sodium carbonate, and well rinsed with clean water. The next step is the preparation of the bleaching liquor.

Preparing the Bleaching Liquor.—To every 100 parts (by weight) of water, which must be free from iron, add 0·675 part of commercial sulphuric acid, stirring this well in, and then sprinkle 0·5 part of sodium peroxide in small quantities into the liquid, taking care that the whole of the peroxide is dissolved completely.

The resulting liquor has a faintly acid reaction, and must be rendered alkaline to red litmus paper by the addition of pure potassium silicate (water-glass) before the goods are entered.

The temperature of the bleaching liquor should be raised to 122-131° F. and maintained thereat for three to five hours, by which time the bleaching will be complete.

The goods are next thoroughly rinsed, then soured with a little acetic acid or sulphuric acid, and rinsed thoroughly again with clean water, followed by sulphuring if desired.

During the bleaching process the reaction of the bath should be tested at intervals by means of red litmus paper (which should turn blue on immersion in the liquor), and if found to be acid must be rendered alkaline again by a fresh addition of potassium silicate.

The bleaching liquor is usually not quite exhausted by one operation, and may be used for bleaching, or fore-bleaching, a second, or even third, batch of goods.

The above bleaching liquor forms a ½ per cent. solution of sodium peroxide. For a 1 per cent. solution the quantities of acid and peroxide must be doubled; and so on in proportion for still stronger solutions. In adding the potassium silicate to make the liquor alkaline care must be taken to prevent the undiluted silicate from coming in contact with wool, since it corrodes the fibre; and this risk is also incurred when the liquor is too strongly alkaline. In the after treatment of the bleached goods it is advisable to work them in a soap bath, charged with a good textile soap.

Drying the Goods.—This operation should be conducted in a well-ventilated room at a temperature not exceeding 113° F., experience having shown that wool bleached in the most effectual manner is damaged considerably by drying in rooms that are too hot or insufficiently ventilated.

In many cases a 1 per cent. sodium peroxide solution is advisable for bleaching, 20 parts by weight of wool being treated with the quantity of liquor specified above; 1½ per cent. of potassium silicate (sp. gr. 1·35) is usually sufficient to render the liquor alkaline.

Magnesium Sulphate in Bleaching Liquor.—Sulphuric acid may be replaced by an equivalent quantity of magnesium sulphate (free from chlorine), the goods being entered into water at 86° F. containing an amount of magnesium sulphate equal to 30 per cent. that of the goods. After remaining a short time in this liquor the goods are taken out, and 10 per cent. of sodium peroxide (calculated on the weight of the goods) is slowly added to the liquor. The goods are then re-entered, and left in the bath, at a temperature of 122-140° F., for two to three hours, after which they are taken out again, rinsed in water acidified with sulphuric acid, and then in clean water.

When sodium peroxide is used in conjunction with magnesium sulphate the reaction proceeds in accordance with the equation:—

$$4MgSO_4 + 4Na_2O_2 + 7H_2O = 4Na_2SO_4 + MgO(OH)_2 . 3Mg(OH)_2 + 3H_2O_2,$$

sodium sulphate, hydrogen peroxide and magnesium perhydroxide being formed. The last-named compound is particularly important in the case of goods that are difficult to bleach, owing to its comparative stability when heated.

Bleaching Silk.—The amount of sodium peroxide used for silk is 12 per cent. instead of 10 per cent., whilst 30 per cent. is used for tussah silk. The liquor is heated to 167-194° F. for this material; but in other respects the operation is conducted in the same manner as for wool.

Articles of white silk, such as ribbons, etc., can be effectually cleaned and bleached by the following method: The goods are first scrubbed with a lukewarm solution of soap, and then washed in warm water. The bleaching liquor into which they are next entered is prepared by dissolving 200 parts (by weight) of magnesium sulphate in 18,000 parts of cold distilled water, 56 parts of sodium peroxide being stirred gradually and carefully into the solution, and followed by 72 parts of sulphuric acid. The liquor should be faintly alkaline, and maintained at a temperature of about 167° F., the goods being left in it for three to four hours and moved about from time to time. After removal from the bath the goods are placed in lukewarm water, acidified with sulphuric acid and containing a little blue dye. Before being ironed smooth the goods are finally passed through a solution of gelatine containing a little acetic acid.

Bleaching Linen, Cotton, Jute and Ramie Goods.—According to a patented French process, linen, cotton, jute and ramie goods may be bleached with sodium peroxide in the following manner: A bleaching liquor is prepared by mixing 8 parts of caustic soda, 1 part of sodium silicate and 1 part of sodium peroxide, 1 part of the mixture being dissolved, slowly and in small portions, in 150 parts of cold water. The resulting liquor is poured over 25 parts, by weight, of linen goods in a bowking kier, which is then filled up with water, closed and gently warmed for three to four hours. This causes a gradual liberation of oxygen from the peroxide, the impurities in the linen fibres being thereby oxidised and bleached, whilst the alkali saponifies any fatty matters present. Finally the goods are washed, and chemicked with bleaching powder if necessary. This method is said to give better results than the older processes.

The Gagedois Bleaching Process.—In 1900 Gagedois took out a patent in Germany for the bleaching of vegetable fibres in a bath of alkali peroxide (Na_2O_2 or K_2O_2), containing an addition of white soap, starch, gum or resins. These latter ingredients were intended to envelop the fibres and protect them from too energetic or rapid action on the part of the oxygen.

To prepare the bleaching liquor a sufficient quantity of clean water is taken to soak 100 parts by weight of goods, and this water is used to dissolve ½-3 per cent. of potassium or sodium peroxide, followed in turn by ½-4 per cent. of ordinary white soap, and 2-8 per cent. of potassium or sodium carbonate or silicate, or else salts of magnesium or alumina. The soap, carbonate, silicates, etc., may be replaced, wholly or in part, by starch, gums or resins that are soluble in warm alkaline liquor. The material to be bleached is exposed to the bleaching liquor for four to six hours in a closed kier, the temperature being maintained at 122-212° F., according to the nature of the goods and the composition of the liquor.

Production of Peroxides.—A. Krause in 1905 applied for a German patent for the preparation of peroxides from sodium peroxide and magnesium sulphate, the liquor being treated with ammonia salts, and the liberated ammonia expelled as quickly as possible by the passage of a current of air devoid of carbon dioxide, or by the aid of a vacuum. By using a concentrated solution of magnesium sulphate, and then quickly drying the freshly precipitated product, without any previous washing, it is stated that preparations can be obtained containing about 27 per cent. of magnesium peroxide (MgO_2).

According to the method of Kirchhoff and Neirath, peroxides of the alkaline earths (MgO_2,CaO_2) can be prepared by decomposing sodium peroxide with a strong organic or mineral acid (added by degrees), which furnishes hydrogen peroxide containing sodium salts, *e.g.*, sodium sulphate when sulphuric acid is used. This solution is allowed to react on suitable metallic hydroxides, metallic oxides or metallic salts, in presence of ammonia, and furnishes fine, granular peroxides distinguished by a high degree of purity. Magnesium perhydroxide (MgO $(OH)_2$) is sold as a bleaching powder (German Patent 74,113); and peroxides prepared by the above process are still finding technical application. A number of products of divergent composition are sold as bleaching soda, one of them (adapted for bleaching cotton) consisting of sodium silicate, water and ammonia-soda.

For bleaching straw and other materials, sulphuric acid is replaced by oxalic acid in the preparation of the bleaching liquor.

Bleaching Feathers.—Ostrich and other feathers must be cleaned, before bleaching, in the usual way, by washing them in a warm soap solution, removing fat by the aid of ammonia and water (very dilute), and should be then entered in a bleaching liquor prepared in the following manner:—

Seventy-five parts of pure crystallised magnesium sulphate are dissolved in 5,000 parts of cold water, 25 parts of sodium peroxide being then added by degrees, with constant stirring. When the peroxide is dissolved, 1,000 parts by weight of the cleaned feathers (22 lb. to 11 galls.) are entered in the bath, worked about at frequent intervals, and left for about twenty-four hours, to bleach them sufficiently. The liquor should not be warmed. The feathers are then taken out, rinsed with water, and immersed for one to two hours in water containing ¼-½ per cent. of crystallised tartaric or oxalic acid, this treatment being succeeded by thorough rinsing in clean water until the acid reaction has disappeared. As already remarked, the operation must be performed in wooden or earthenware vessels, not metal. If the bleaching liquor is not completely exhausted, it may be used in fore-bleaching.

Sodium Peroxide in Washing Powder.—Sodium peroxide is also used as an ingredient of washing powders and the like, which are sold under a variety of fancy names. A sodium peroxide soap is sold as "Pernatrol".

In determining the value of sodium peroxide, the chief criterion in most cases is the amount of oxygen it is capable of liberating, no matter whether such oxygen originates in sodium peroxide or higher oxides. According to R. Lasker, the Archbutt-Grossmann gas-volumetric method is the only one suitable for determining the "active" oxygen present in sodium peroxide, the methods employing permanganate for titration being unreliable. The iodometric method of Rupp also furnishes merely approximate results.

Barium Peroxide.—Barium peroxide (BaO_2) is a white mass, prepared by heating barium oxide (BaO) to dark redness in the air or in oxygen. When treated with dilute sulphuric acid in the cold, barium peroxide furnishes hydrogen peroxide, the white precipitate of barium sulphate formed at the same time being separated by filtration:—

$$BaO_2 + H_2SO_4 = BaSO_4 + H_2O_2.$$

Sulphuric acid may be replaced by hydrochloric acid:—

$$BaO_2 + 2HCl = BaCl_2 + H_2O_2.$$

Before being used for bleaching, barium peroxide, which invariably contains barium hydroxide and therefore has a strongly alkaline reaction, must be washed with cold distilled water.

Bleaching Silk with Barium Peroxide.—Ordinary or tussah silk is sometimes bleached with barium peroxide, two baths being necessary. The material is first placed in an acid bath prepared by dissolving 1 part of hydrochloric acid (20° Bé.) in 1,000 parts of water. This bath must be used at a temperature of 68° F., the silk being left in it for an hour, taken out, wrung, and entered in the barium peroxide bath. This latter is prepared by mixing up to 10 per cent. of barium peroxide (based on the weight of goods to be treated) with the amount of water necessary for working the materials. The working temperature of this bath is 140° F., and the silk must be treated for one hour, the series of operations being repeated if necessary.

CHAPTER III.

PERBORATES.

SALTS of Perboric Acid.—The perborates are salts of perboric acid. This acid, which has not yet been isolated, differs from boric acid in containing an extra atom of oxygen.

A number of perborates are known, all of them being very stable, even when they contain one or more molecules of water of crystallisation, though the application of heat or a trace of water of solution is sufficient to cause their decomposition. Like the peroxides, they part with the surplus molecule of oxygen, which combines, in the nascent state, with water to form hydrogen peroxide.

Properties of the Perborates.—J. Brahat and H. Dubois have thoroughly investigated and reported on the properties of the perborates, the most important, for our purposes, being the following: On treatment with cold concentrated sulphuric acid, the perborates furnish highly concentrated hydrogen peroxide, which decomposes at once with liberation of ozone. They liberate iodine from potassium iodide, and furnish perchromic acid with bichromate and sulphuric acid. When added to sulphuric solutions of titanic acid or vanadic acid, perborates produce a deep blood-red coloration. They decompose permanganate ($KMnO_4$), which forms a reagent by means of which their content of active oxygen can be determined with ease. As carriers of oxygen the perborates are well adapted for converting lower oxides to a higher stage of oxidation, ferrous salts being converted into ferric salts, the sesquioxide being thrown down from an alkaline solution, Copper oxide and cupric salts are converted into peroxide, which immediately decomposes with liberation of oxygen, whilst cuprous salts combine with perborates to form insoluble, stable salts. The perborates of calcium, magnesium, strontium, barium and zinc have also been prepared; but their composition was not uniform, varying according to the conditions of the experiment.

Ammonium Perborates.– Several ammonium perborates have been prepared, one of them, with the formula NH_4BO_3, H_2O, containing 16·84 per cent. of active oxygen.

Sodium Perborates.—The sodium perborates have been more exhaustively studied than any others. Brahat and Dubois obtained salts of varying composition by electrolysing a solution of sodium orthoborate, or by precipitating with alcohol a solution of sodium borate in hydrogen peroxide. They described a compound $NaBO_3$, $4H_2O$; and also a tri-, bi- and monohydrate ($NaBO_3$, H_2O). The last named is very stable, and contains 16 per cent. of active oxygen.

The monohydrated compound is soluble in water to the extent of 25 parts per 1,000 at 20° C., the solution behaving just like free hydrogen peroxide. The solubility of this compound is increased by the presence of boric, tartaric or citric acid: and the solubility is relatively much higher in glycerine.

Anhydrous sodium perborate has also been prepared by prolonged desiccation *in vacuo* over phosphorus pentoxide. This salt, too, is very stable, retaining 17 per cent. out of 19·51 per cent. of active oxygen after storage for eighteen months.

Perborax.—G. F. Jaubert obtained a "Perborax" by mixing 238 parts by weight of boric acid with 78 parts of sodium peroxide, and introducing the mixture into 2,000 parts of water. The resulting solution quickly deposited a snow-white crystalline flour of the formula $Na_2B_4O_8$, $10H_2O$, and containing 4·17 per cent. of active oxygen. Perborax is far more soluble than the sodium perborates, 1,000 parts of water dissolving 42 parts at 11° C., 71 parts at 22° C., and 138 parts at 32° C. Free hydrogen peroxide is present in the solution without any addition of sulphuric acid. On recrystallisation a part of the compound is transformed into $NaBO_3$, $4H_2O$, which salt is also obtained from perborax on saturating one-half of the sodium in the same with a mineral acid.

Jaubert has patented a process (1906) for the preparation of sodium perborate ($NaBO_3$, $4H_2O$) on a technical scale. For this purpose concentrated sulphuric acid (free from arsenic and iron) is mixed with water and treated with a mixture of sodium peroxide and powdered boric acid, the temperature being prevented from rising above 20° C. (68° F.). After leaving to stand for several hours, the deposited precipitate is filtered off, washed with cold water and dried in the air. In another process by the same inventor, sodium perborate is prepared by the action of boric acid and hydrogen peroxide on sodium peroxide, 500-600 parts of 30 per cent. hydrogen peroxide being mixed with 200 parts of water, whereupon 124 parts of powdered crystallised boric acid are stirred in thoroughly, and followed by the gradual addition of 29 parts of sodium peroxide in the form of powder. The temperature should not exceed 20° C. throughout the operation. The sodium perborate, which is formed in accordance with the equation: —

$$2B(OH)_3 + Na_2O_2 + H_2O_2 + 4H_2O = 2(NaBO_3, 4H_2O)$$

is soon deposited as a white, crystalline powder, which is filtered off at the end of an hour, washed and dried.

Merck's Sodium Perborate.—A sodium perborate prepared by this maker ($NaBO_3$, $4H_2O$) forms white crystals, which are soluble to the extent of 25 per cent. in water at 20° C. The preparation is pure and is perfectly white, containing about 10 per cent. of active oxygen, or twice as much as Jaubert's "Perborax" mentioned above.

Merck's sodium perborate unites the properties of hydrogen peroxide and normal sodium borate (borax). Dilute acids liberate hydrogen peroxide; and concentrated sulphuric acid produces decomposition, with liberation of ozone. Oxygen is given off when the aqueous solution of the perborate is warmed to 60° C. (140° F.), or treated with mineral or organic catalysators, ferments, animal tissues, etc. The differentiation of borax from sodium perborate can be effected by means of potassium chromate, a blue coloration being produced when sodium perborate is present, but none at all in the case of borax.

The method patented by the Deutsche Gold und Silberscheideanstalt, Frankfurt-on-Main, consists in introducing 1,500 parts of sodium peroxide into 3,000 parts of water, sufficient ice being added to prevent any rise in temperature. Waste gases containing carbon dioxide, but free from dust, are passed through the solution until no free alkali is left, an excess of carbon dioxide being uninjurious. A concentrated solution of sodium metaborate, prepared from 1,240 parts of boric acid and 240 of caustic soda, is next added, the deposition of sodium perborate being facilitated by stirring. By adding ice, if necessary, care is taken to prevent the final temperature of the liquid from rising above 2° C. (35½° F.), and that the volume of the liquid is sufficient to maintain all the soda in solution. The precipitated perborate is separated and dried in the usual way. The sodium metaborate may be replaced by an equivalent quantity of borax or other alkali borate.

According to Jaubert, the sodium perborate prepared by the Société d'Oxylithe, Paris, is excellently adapted for the production of pure hydrogen peroxide. This perborate crystallises from aqueous solution at 30° C. as somewhat voluminous lustrous prisms; the solution has a decidedly alkaline reaction, and behaves like free hydrogen peroxide in presence of potassium permanganate. Above 40° C. decomposition begins, accompanied by liberation of oxygen; but the loss is only slight up to 60° C. Between 15° and 32° C. the solubility of the salt is about 25·5-37·8 grms. per litre, though more concentrated solutions can be obtained by the addition of acids.

A solution containing over 30 per cent (by volume) of hydrogen peroxide, and suitable for technical uses, can be obtained with sulphuric acid. A 10 per cent. solution quite as active as ordinary hydrogen peroxide can be prepared by dissolving 170 parts by weight of sodium perborate and 60 parts of pure citric acid in 1,000 parts of water. After decomposition there remain: sodium metaborate and sodium biborate, or boric acid and the salt of the added acid (*i.e.*, sodium sulphate or citrate, according as sulphuric or citric acid has been used).

The sodium perborate of the Société d'Oxylithe exhibits the same general properties as that of Brahat and Dubois ($NaBO_3$, H_2O), of which latter 25 grms. will dissolve per litre of water at 20° C. The hydrogen peroxide solution prepared with sodium perborate is specially adapted for bleaching fine goods on account of its purity.

Sapozon.—A perborate soap that disengages oxygen is sold under this name, and acts as a disinfectant and bleaching agent. Sodium perborate becomes the source of the oxygen, the soap is free from corrosive properties, the decomposition product being ordinary borax (and not caustic soda, as when sodium peroxide is used).

Testing Sodium Perborate.—Rupp and Mielck give the following equation as expressive of the reaction employed in the determination of sodium perborate:—

$$NaBO_3 + NaIO = NaI + O_2 + NaBO_2.$$

A definite quantity (about 10 grms.) of the well-mixed preparation is weighed out and dissolved in about 50 c.c. of water, about 10 c.c. of 15 per cent. of alkali (either caustic potash or caustic soda) and 25 c.c. of decinormal iodine being then added. At the end of about five minutes, the mixture is acidified (with dilute hydrochloric acid 1 : 1), the unconsumed iodine being titrated with decinormal thiosulphate, in presence of starch solution as indicator.

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CHAPTER IV.

OZONE.

Formation of Ozone.—When experiments are carried on indoors with a statical electrical machine, a peculiar smell, resembling that noticeable out of doors during a thunderstorm, makes itself apparent.

Whenever oxygen or air is subjected to the action of electrical discharges, whether sparks or phosphorescent discharges, the volume of the gas is reduced, and its properties are modified; the resulting product, "ozone," has a characteristic smell, and being far more energetic than ordinary oxygen, has been called "active oxygen". Minute quantities of ozone are present in the air; and a small quantity is formed during the electrolysis of water.

Ozone Generators.—The Siemens ozone tube (Fig. 2) is a device for preparing ozone on a comparatively large scale. It consists of two concentric glass tubes, fused together at the top, the outer tube being provided with an inlet and a discharge tube for the air or oxygen. The inner tube is lined, and the outer tube covered, with tinfoil, thus forming a condenser, the coatings of which are formed by the tinfoil, and the dielectrics by the glass and air. When the coatings are charged with rapidly alternating currents of high tension, ozone is formed in the adjacent air.

It has been found that the production of ozone is greater on the passage of non-luminous discharges through the air than during the passage of sparks. Messrs. Siemens and Halske manufacture ozone by means of these tubes, which are immersed in water instead of being coated with tinfoil, the water playing the part of the coating.

Similar in principle is the Elworthy-Kolle ozone generator, which also operates by the non-luminous discharge of high-tension currents, these being generated by an alternating dynamo (3-4 amperes and 125-135 volts). This current is passed through a small transformer of special design, which transforms it into a 11,000-12,000 volt current. The field of the silent discharges is formed by two metal spirals, one of which is housed in a narrow glass tube, and the other in a wider tube surrounding the first. The air to be ozonised passes through both tubes in succession. From three to ten

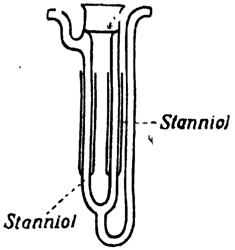

FIG. 2.—Siemens Ozone Tube (Stanniol = tinfoil).

such tubes are connected to form a battery. According to the researches of Dr. Philipp (Stuttgart) with a 10-tube battery, 70 grms. of ozone are produced per kilowatt hour (more recent communications place the amount at 125-145 grms.). The concentration of the mixture of ozone and air averages 0·4-0·5 grm. per cub. metre; but this may be increased by connecting a number of apparatus in series.

Fischer and Massenoz obtain a high yield of ozone by another method. When an electric current is passed through dilute sulphuric acid, a finely tapered platinum wire being used as positive electrode, so that the current density at the extremity is very high, the oxygen liberated at the anode is very rich in ozone. This was demonstrated by MacLeod in 1886. In this arrangement, however, the platinum wire is rapidly consumed. Fischer and Massenez use for the same purpose a thin tube of platinum, cooled by a current of water. The platinum tube tapers to a very fine point (the width at the extremity being only 0·1 mm.), but the metal is kept thoroughly cooled from the inside, despite the high current density and heat.

With this arrangement over 22 per cent. of ozone can be obtained per 1 ampere of current, this yield corresponding to 7 grms. of ozone per kilowatt hour.

Production of Ozone by Chemical Means.—Ozone is produced when fragments of phosphorus, partly covered with water, are left in prolonged contact with air under a bell glass; that is to say, ozone is formed during the gradual oxidation of moist phosphorus. The smell of ozone can be clearly detected after a few hours. The formation of ozone has also been observed in various instances of gradual combustion. Up to the present, ozone has not been prepared in a pure state, but only in admixture with oxygen or air.

Properties of Ozone.—When cooled by means of liquid air, ozone is condensed into a blue liquid, which boils at - 120° C. and is converted into a blue gas. Liquid ozone is extremely explosive, owing to its great tendency to change into ordinary oxygen with disengagement of heat. Gaseous ozone also changes spontaneously into ordinary oxygen, with increasing rapidity as the temperature rises.

Ozone is the most active oxidising agent known; and many oxidations that require heat for their achievement by oxygen will proceed at ordinary temperature in presence of ozone.

The density of ozone is $1\frac{1}{2}$ times that of oxygen. On the assumption that the sp. gr. of gases is proportional to their atomic weights, the molecular weight of ozone is $1\frac{1}{2} \times 32 = 48$, whence it follows that 3 atoms of oxygen are combined together in the molecule of ozone. It is supposed that the third atom is held in a state of comparatively loose combination, which circumstance is held to account for the powerful oxidising (*i.e.*, bleaching) effect of ozone.

Employment of Ozone in Bleaching.—For this purpose air is ozonised on a large scale by electrical means, in order to replace grass bleaching, the other operations remaining the same as practised in the bleaching of flax yarns. The yarn to be bleached must be put through a preliminary treatment with either dilute sulphuric acid or oil of turpentine, etc. It may be mentioned, in this connection, that atmospheric oxygen can be ozonised by placing the air in intimate contact with oil of turpentine,

After the preparatory treatment, the yarn is exposed to the action of the ozone for about seven hours. For generating the ozone, pure air is drawn in by means of suction pumps, and after passing through the ozonising apparatus, is led into the bleaching chambers, where the (not too moist) yarn is suspended in the usual way. The absorption of the ozone proceeds quickly and completely. A single ozone treatment furnishes a three-quarter white bleach, two or three treatments being necessary for complete bleaching. The subsequent operations are the same as after grass bleaching, and the yarn must also be chemicked, a very dilute solution of bleaching powder being, however, sufficient.

According to a method introduced by A. Bourin and F. Aymerie, for washing, scouring and bleaching raw wool, or other raw or manufactured textile materials, ozone is passed, as a continuous current, over the wool, etc., in a vacuum apparatus. The raw material is laid on perforated trays, fabrics being wound on perforated cylinders that are open at one end for the admission of the ozone. It is claimed that the employment of a vacuum greatly strengthens the action of the ozone.

The white obtained by ozone bleaching is of equal purity and character with that from grassing, whilst the operation takes up less time and can be carried on irrespective of the season or weather.

CHAPTER V.

SODIUM BISULPHITE AND HYDROSULPHUROUS ACID.

BLEACHING with Sulphur Dioxide.—The first point to be mentioned in connection with bleaching with sulphur dioxide is that sodium bisulphite ($NaHSO_3$) is frequently used instead of a solution of the dioxide in water. The fibrous material to be bleached is entered in a solution containing sodium bisulphite and hydrochloric acid, the operation being really equivalent to bleaching in a solution of common salt saturated with sulphur dioxide:—

$$NaHSO_3 + HCl = NaCl + H_2O + SO_2.$$

When sulphur dioxide is used for bleaching wool, a colourless compound is formed between the colouring matter of the wool and the dioxide; but as this compound is liable to undergo decomposition after a time, the wool frequently resumes its natural colour after bleaching by this method.

Bleaching Wool with Hydrosulphurous Acid.—Whereas in bleaching fibres with sulphur dioxide, the compounds of the latter with the colouring matter of the fibre have to be got rid of by washing, the use of hydrosulphurous acid ($H_2S_2O_4$) causes, in many cases, the colouring matters of the fibre (wool) to be transformed into colourless bodies, which do not revert to their original condition on exposure to the air.

Sodium Hydrosulphite.—A similar result is produced when very yellow wool is treated with a solution of sodium hydrosulphite ($NaHSO_2$) followed by the addition of thin milk of lime until the reaction becomes slightly alkaline. When bleaching is finished the wool is rinsed with cold water, then treated with very dilute acetic acid, and finally washed again. In this process the wool is not washed with warm sodium carbonate or soap solution, as is usual in bleaching with sodium hydrosulphite (with a little very finely ground indigo). The indigo is converted by the hydrosulphurous acid into indigo white, and is absorbed by the fibres in this condition, the blue colour being regained on exposure to the air. In this way the natural yellow tint of the wool is permanently removed.

Properties of Sodium Bisulphite.—This salt, which forms white crystals that decompose on being heated in the air, is usually sold in the form of a colourless or pale yellow (traces of iron) solution, smelling of sulphur dioxide; and it keeps well if stored in closed vessels. A solution of about 35° Bé. density contains 22-23 per cent. of sulphur dioxide.

As mentioned above, gaseous sulphur dioxide for bleaching is frequently replaced by a solution of sodium bisulphite containing hydrochloric acid, this being used, for instance, in bleaching straw.

Sodium sulphite (Na_2SO_3 $7H_2O$), which is also met with in commerce, can be used like the bisulphite, but is less frequently employed.

Saget's Bleaching Process.—According to Saget, cotton goods can be bleached with sodium sulphite, or bisulphite, and Turkey-red oil, by the following method:—

The sulphite is stirred into milk of lime, slaked lime being mixed with its own weight of Turkey-red oil and the necessary quantity of water, sodium sulphite of 30° Bé. density (equal in weight to the lime) being then added. The resulting liquid has a milky appearance. The goods are padded with this liquid, at about 120-140° F., then steamed for one and a half to two hours, washed in hot water, soured in lukewarm dilute acid for an hour out of contact with air, slightly chemicked, rewashed and dried.

It will be observed that the bleaching action does not take place immediately, but only after souring and when the goods have been left in a heap for two to three hours. If they are washed at this stage, and lightly chemicked, a good white is obtained.

Thierry, Mieg & Co.'s Bleaching Process.—In the *Dyer and Calico Printer* (1906, p. 87), Thierry, Mieg & Co. described a new process by means of which woollen piece-goods can be bleached more quickly, cheaply and completely than heretofore. The jigger is replaced by the dye vat, and no soap is used, thus saving, not only the cost of the latter, but also avoiding the formation of lime soaps, and consequent contamination of the goods when hard water is used.

For six lengths of wool muslin, 4½ lb. of Solvay soda, or an equivalent weight of soda crystals, are dissolved in the dye vat. The pieces are entered in the solution, at 104° F., for half an hour, and are then washed in the vat with water at the same temperature, and drained in the hydroextractor. Next they are padded with a solution of sodium bisulphite (6° Bè.) steamed without pressure for 45-60 seconds, and washed in the vat with warm water. The goods are now ready for chemicking, which has replaced the treatment with sodium stannate. The method is cheap, and gives a sufficient white for printed goods.

Flannel is bleached by the same process, but by the aid of five passes in the jigger: (1) Six pieces of flannel are passed through an aqueous solution of 2¾ lb. of soda crystals at 104° F.; (2) passage through lukewarm water; (3) passage through a solution containing 11 lb. of carbonate of soda; (4) washing in lukewarm water; (5) passage through a solution of sodium bisulphite (6-7° Bé.).

Experiments have shown that this process, which is cheap and prevents the formation of lime soaps, is, like the soap process, equally as good for printed goods as for white articles. It is specially recommended for producing a quick white on goods intended for printing.

Bleaching Manila Hemp.—Sodium bisulphite is suitable for bleaching Manila hemp. The fibres must first be cleansed by a gentle boiling for about three hours in a 4 per cent. solution of carbonate of soda, or caustic soda of similar strength for a shorter time (two to three hours). With the caustic alkali the hemp parts with some of its colouring matter during the boiling, the liquid turning pale yellow. The cleaned and washed hemp is then entered in a bleaching bath of sodium bisulphite solution, where it remains for about twelve hours. The fibres, which are now quite white except at the points of attachment, are carefully washed, and when dried will exhibit their original lustre and strength.

After-treatment with Bisulphite.—A solution of sodium bisulphite (7° Bé.) is used for the after-treatment of jute that has been bleached with permanganate or bleaching powder. The same treatment may also be applied to other bleached vegetable fibres, and to wool bleached with permanganate. The details will be given later, in connection with the permanganate process.

Sulphur dioxide, or sodium bisulphite, is used for bleaching straw and leather, in addition to wool and a number of vegetable fibres.

Bleaching Straw.—To bleach straw plait, straw hats, etc., the material is soaked and washed in soap and water, which may contain, if necessary, an addition of ammonia (1¾ lb. per 100 galls.), to serve as a detergent. After being well rinsed with clean water and slightly dried, the damp goods are entered for several hours in a solution of sulphur dioxide, or preferably sodium bisulphite, sufficient being used to cover them completely. When sufficiently bleached, they are transferred to a solution of tartaric acid (or dilute hydrochloric acid) in a separate vessel, and are left there until the requisite whiteness has been attained. A thorough rinsing completes the process.

A novel feature in this process, which in itself is old, consists in the use of a specially prepared soap for the preliminary treatment of the material. The soap is a potash soap, salted out with dilute caustic lye and common salt, and mixed, whilst still in the soft condition, with one-fifth of its own weight of ground sodium sulphite (normal sulphite, Na_2SO_3). The soap is cut into bars, whilst soft, and dried. It is highly suitable for cleansing the goods in question.

Bleaching Leather.—In Börntrager's process, the leather, as is well known, contains considerable quantities of fat and tannin; these impurities must be removed before bleaching can begin. With this object the leather is digested for an hour, at 104° F., with benzol, drained, freed from the residual benzol by warming in a water-jacket apparatus, and then treated with liquid sulphurous acid (dissolved sulphur dioxide). This process gives a light pinkish white product which, when carefully dried, can be used for fine work.

CHAPTER VI.

DISCHARGING COLOUR FROM TEXTILE FABRICS WITH HYDROSULPHUROUS ACID.

CASSELLA'S Old Process.—According to Cassella's patent, the discharge of colour for textile fabrics was effected by soaking the articles (*e.g.*, clothing) in a sufficiently strong cold or lukewarm bath of sodium hydrosulphite ($NaHSO_3$) for two to four hours, or overnight. The bath should be set in a closed vessel, adapted to be warmed towards the end of the treatment. The goods were finally rinsed in water, and were then ready to be re-dyed.

Preparing the Discharge.—The preparation of the hydrosulphite discharge liquor, which was claimed to discharge even fast organic dyes completely, without injury to the fibre, was generally carried out by the user. For this purpose, 1 part of zinc dust was slowly added to a mixture of 10 parts of commercial bisulphite (35° Bé.) and 10 parts of cold water, and stirred, the liquid being then left for a short time to clear.

The reaction is explained by the equation:—

$$3NaHSO_3 + Zn = NaHSO_2 + Na_2SO_3 + ZnSO_3 + H_2O.$$

That is to say, the sulphurous acid of the sodium bisulphite is reduced to hydrosulphurous acid, sodium hydrosulphite, sodium sulphite and zinc sulphite being formed.

Discharging Colour from Shoddy and Dyed Fabrics.—To discharge colours from shoddy and dyed fabrics, 4-6 gallons of the above hydrosulphite and ½ gallon of acetic acid are added to 100 gallons of water, the goods being entered and worked about in the liquor at a temperature of 120-140° F., for a quarter to half an hour, till the colour has lightened sufficiently. In this way a considerable number of dyes can be discharged, or at any rate weakened. The goods are then rinsed immediately, lightly soured with sulphuric acid and rinsed again.

The hydrosulphite solution is very soon exhausted, especially at higher temperatures, so that it should be freshly prepared and added to the bath shortly before use.

Stable Hydrosulphite.—Owing to the instability of the hydrosulphite prepared in the above manner, it has latterly been superseded by a more stable preparation. A stable zinc hydrosulphite, in the form of paste, was employed at one time, but this did not become popular, and gave place to a chemical combination of hydrosulphite and formaldehyde, which was found to answer in practice.

Method of Using Hydrosulphite.—At present there are three forms of hydrosulphite on the market: zinc hydrosulphite, calcium hydrosulphite and formaldehyde hydrosulphite. These are chiefly used as discharges in calico printing, etc., a process analogous in principle to the one now under consideration, being effected by the reduction of the dyestuffs. The hydrosulphites also find employment in the prevention of colours from running, in the processes of milling, washing, soaping, etc., by rendering harmless the insufficiently fixed dyes that would otherwise run into and spoil the lighter coloured or white portions of the fabric. This object is attained by simply adding a little hydrosulphite to the baths. The quantity of hydrosulphite (and formaldehyde) required to give a pure white on dyed woollen and cotton fabrics, depends on the resistance of the dyes in question to the reducing action of the hydrosulphite.

Eradite.—A solid preparation of sodium hydrosulphite, sold under the name of "Eradite" is used for reducing indigo.

Cassella's Hyraldite.—Cassella & Co. put on the market, under the name "Hyraldite," a highly stable compound of hydrosulphite and formaldehyde, in the form of a white mass, which is readily soluble in cold or hot water. In contrast to hydrosulphite, the solution is very stable, in the cold or hot state, when neutral or alkaline. On being treated with bisulphite, acetic acid or any other acid, however, it furnishes hydrosulphite, which exerts an energetic reducing action.

Discharging with Hyraldite.—This last-named property forms the basis of the application of Hyraldite A for discharging the colour of dyed materials.

The operation is preferably carried out in wooden vats, the lukewarm bath being charged with 5 to 10 per cent. of Hyraldite A and 5-10 per cent. of acetic acid, the proportions being calculated on the weight of the goods. The material to be discharged is entered and worked about while the temperature is being slowly raised to boiling-point (½-¾ of an hour), boiling being continued for another quarter of an hour.

The acetic acid may be replaced by an equal quantity of sodium bisulphite (35° Bé.).

The treatment is followed by rinsing, souring and a final rinsing.

As already mentioned, the amount of hydrosulphite required depends on the depth and fastness of the colouring matter to be discharged, and the degree of decoloration desired. A second mark, Hyraldite W, is specially adapted for completely discharging numerous dyes. Both marks should be kept in tightly closed vessels in a cool place.

Increasing the Discharging Effect.—Cassella & Co. subsequently patented a process for increasing the discharging effect of formaldehyde hydrosulphite. This result is obtained by adding metallic oxides or carbonates (*e.g.*, of zinc or magnesium) to the discharge liquor. This addition is said to render the hyraldite discharge applicable to discharge printing on woollen goods, for which materials it was previously imperfect.

Meister Lucius & Brüning's Stable Hydrosulphite Compounds.—The Farbwerke vorm. Meister Lucius & Brüning patented methods for preparing stable compounds of hydrosulphites and ketones, and for a sparingly soluble zinc-formaldehyde sulphoxalate. The former compounds are obtained by treating hydrosulphites with ketones (acetone, methylethylketone) in presence of alkalis, caustic soda and ammonia being preferably used together.

Acetone hydrosulphite, for instance, will stand a temperature of 132° F., or a sojourn of several weeks in the warm, without suffering any serious loss of activity; that is to say, it will withstand the influence of conditions under which the best hydrosulphite preparations previously known would certainly have decomposed much more speedily.

The zinc-formaldehyde sulphoxalate is prepared by acting on zinc dust with sulphuric acid, treating the solution with 38 per cent. formaldehyde, and neutralising the resulting solution of zinc-formaldehyde hydrosulphite with carbonate of soda. It forms a sparingly soluble crystalline compound, which will keep unaltered in the air, and furnishes sodium-formaldehyde sulphoxalate when digested with carbonate of soda solution.

CHAPTER VII

PERMANGANATE

ALTHOUGH the permanganate process has long been in use, especially for bleaching fibrous materials, it must be included among modern bleaching agents, owing to the various improvements it has sustained. It is applied not merely to the bleaching of vegetable fibrous materials, especially jute, but also for bleaching wool and silk.

Bleaching with Permanganate.—The materials to be bleached are treated in a damp state with a cold solution of potassium permanganate, of 5 to 8 per cent. strength, according to the nature of the material under treatment. The solution is reduced very quickly, forming manganese dihydroxide, which stains the fibre or fabric brown.

Action of Permanganate.—The employment of permanganate for bleaching rests on its oxidising action, the solution yielding up colour-destroying oxygen to organic substances, the above-mentioned insoluble manganese dihydroxide (MnO_2, H_2O) being precipitated.

A few minutes are usually sufficient for the reduction of the permanganate, the time varying with the character of the material under treatment. The simplest plan is to take a sample of material out of the bath after a few minutes, and ascertain whether a corresponding quantity of the hydroxide has been deposited.

Bleaching Wool or Silk.—In bleaching these materials, a little magnesium sulphate is added to the permanganate bath, on account of the formation of caustic potash during the decomposition of the solution. After removal from the bath, the materials are treated with a cold, dilute solution of sodium bisulphite, to remove the brown stain, after which they are washed in slightly acid water, followed by clean water, and then dried.

The bleaching action of the permanganate only becomes apparent on treating the stained material with sodium bisulphite or sulphur dioxide. The powerful reducing action of this reagent converts the manganese dioxide into manganese protoxide, the sulphurous acid being at the same time oxidised to sulphuric acid, with which the manganese protoxide forms the readily soluble and almost colourless salt, manganous sulphate, which can easily be removed by washing.

The potassium permanganate solution can also be used, together with a little sulphuric acid, in the cold. In this case the material is not stained brown, since the manganese dioxide formed is at once converted into soluble manganous sulphate. Here the bleaching action of the permanganate is supplemented by that of the oxygen liberated by the decomposition of the dioxide.

Addition of Magnesium Sulphate to the Bleaching Liquor.—This addition, referred to above as necessary, in bleaching wool or silk, on account of the formation of caustic potash during the decomposition of the permanganate, neutralises the alkali, with formation of neutral potassium sulphate and insoluble magnesium hydroxide. Hence no injury can accrue to the fibre.

In bleaching cotton (yarn or fabrics), linen, jute, or any other vegetable fibrous materials, the addition of magnesium sulphate may be omitted.

Another method of bleaching with permanganate consists in rinsing the material, on which the hydroxide has been deposited, and then treating it for about ten minutes with a very dilute solution of hydrogen peroxide. This treatment is followed by soaking in slightly acid water, until the manganese compound has been dissolved, the material being afterwards thoroughly washed.

In this method the manganese dioxide decomposes the hydrogen peroxide, by simple contact, into water and oxygen, the latter exerting a bleaching action in its nascent state.

In the after treatment the water is acidified with sulphuric acid, in order to convert the manganese protoxide (formed from the dioxide) into the readily soluble manganous sulphate.

Strength of Permanganate Solution.—Instead of the solution mentioned above a 2½ per cent. solution of permanganate may be used, the material being left in the bath for a proportionate time (about two hours), and good results can be obtained with still weaker solutions, if used lukewarm. This modification (with a little magnesium sulphate) is advisable in bleaching wool, the material being afterwards treated with sodium bisulphite.

As mentioned above, stronger solutions may be used for coarser vegetable fibrous materials; weaker, cold solutions being employed for finer goods.

The permanganate process is not infrequently used for bleaching fine jute yarns; but as a rule jute is bleached with sodium hypochlorite solution, after a preparatory treatment with alkali silicate, the bleached goods being afterwards treated with a 2 per cent. solution of sodium bisulphite.

New Process for Bleaching Jute.—According to a newer process jute yarn is first treated with a solution of carbonate of soda at 149° F., and after being drained is immersed in a 5 per cent. solution of potassium permanganate. At the expiration of half an hour the goods are taken out and worked in dilute hydrochloric acid, containing a little sodium bisulphite or hydrogen peroxide, followed by washing in clean water.

To make the goods still whiter the operations should be repeated. In this process the jute loses about 3-4 per cent. in weight.

A first-class white, which will not alter on exposure to the air, can be obtained with the permanganate process, by first treating the suitably cleaned jute (or other vegetable fibrous material) for some time (three to four hours) in a solution of sodium hypochlorite (2° Bé.) before entering in the permanganate bath. After wringing and rinsing, the goods are soured in a weak acid bath, preferably of acetic acid.

After wringing, the jute is steeped for an hour in a 1½ per cent. solution of potassium permanganate and then thoroughly washed. The material, which is stained brown, is entered in a bath of sodium bisulphite, prepared from 950 parts of water and 50 parts of bisulphite (38° Bé.), and is left there for about three-quarters of an hour. The bleached material is thoroughly rinsed and then entered in a soap bath, consisting of a ½ per cent. solution of soap with a little ultramarine water-blue or methyl violet to improve the white. In this bath the jute is treated for fifteen to twenty minutes, and acquires an improved lustre.

Bleaching Skins.—Sheepskins to be used for rugs, etc., must be washed, drained and dressed before bleaching, the dressing process usually consisting of a treatment with alum, salt, carbonate of soda and soap solution. The dressed skins are stretched on wooden frames and then bleached. The permanganate process may be used, though it is not so reliable as the peroxide process (sodium peroxide) previously mentioned. The skins are laid in pairs (woolly sides out) in a ½ per cent. solution of permanganate until they have acquired a deep brown stain, whereupon they are removed, drained, washed and placed in a strong bath of sulphurous acid (dissolved sulphur dioxide) until the wool is pure white.

These two operations are preferably carried out quickly, so that the skins are not left too long in the liquor. The final treatment consists in washing the skins in dilute sulphuric acid and then carefully in lukewarm water.

Bleaching Straw.—Of the numerous methods applied to the bleaching of straw, the permanganate process is worthy of mention as the simplest. The straw is placed lengthwise in successive layers in a suitable trough, where boiling water is poured over it. The straw is left in the water for ten to twelve hours altogether, being treated at intervals with brine. Boiling water is added after each treatment. According to the degree of purification attained, the straw is next entered in a 1-5 per cent. bath of soap at 76° C. (169° F.) and kept therein at about the same temperature for two to four hours. Next follows rinsing with warm water, draining (preferably in a machine) and drying in a room at a temperature not exceeding 26° C. (79° F.)

To dispense with the soaking in boiling water the soap bath must be used stronger (about 3·5-6 per cent.), and the straw left in it for a longer time (about six hours) at the temperature specified. After taking it out of the soap liquor the straw is suitably rinsed with lukewarm water and placed in a 10 per cent. solution of potassium permanganate, where it is left for twenty minutes and is then transferred at once to a 6·7 per cent. solution of sodium hypochlorite ($Na_2S_2O_3 + 5H_2O$). This solution must contain 2·2-6·6 per cent. of hydrochloric acid, added shortly before the fully bleached straw is taken out. Rinsing and drying complete the process.

Bleaching Ivory.—The permanganate process may be applied to bleaching ivory. For this purpose the ivory is placed for half an hour in a 0·4 per cent. solution of potassium permanganate, and is then taken out and well rinsed, to be next transferred to a 10 per cent. solution of oxalic acid, also for half an hour. After washing, the cycle of operations is repeated as often as necessary to obtain the desired effect. Finally the ivory is left for a short time in a hot mixture of lime, bran and water, then rubbed over with perfectly dry sawdust and exposed for a long time to the influence of sun and air. In connection with this process it should be noted that part of the oxalic acid, on coming in contact with manganese dioxide, is decomposed, with liberation of carbon dioxide. With manganese protoxide, oxalic acid forms a sparingly soluble, colourless salt, which is soluble in strongly acid liquids only.

CHAPTER VIII.

HYDROGEN PEROXIDE.

Constitution and Properties.—Hydrogen peroxide, H_2O_2, contains twice as much oxygen as water, and has a great tendency to decompose into water and oxygen, as expressed by the equation :—

$$\underset{\text{Hydrogen peroxide}}{2H_2O_2} = \underset{\text{Water}}{2H_2O} + \underset{\text{Oxygen}}{O_2}.$$

Now compounds that readily part with oxygen are termed oxidising agents; and hydrogen peroxide is included in this category. At the moment of its liberation from a compound, oxygen exerts a powerful oxidising and bleaching effect; and this is the case with the oxygen set free by hydrogen peroxide.

Preparation of Hydrogen Peroxide.—Hydrogen peroxide is prepared by placing barium peroxide in cold dilute sulphuric acid—insoluble barium sulphate and an aqueous solution of hydrogen peroxide being formed. The reaction is expressed by the equation :—

$$\underset{\text{Barium peroxide}}{BaO_2} + \underset{\text{Sulphuric acid}}{H_2SO_4} = \underset{\text{Barium sulphate}}{BaSO_4} + \underset{\text{Hydrogen peroxide}}{H_2O_2}.$$

By distilling this solution in a partial vacuum the water can be driven off first, and nearly pure hydrogen peroxide is obtained, as an oily fluid from which the pure, crystalline peroxide can be prepared.

According to P. Courey the best and simplest method of preparing hydrogen peroxide is from barium peroxide and hydrofluoric acid. It may also be obtained from perborates, persulphates and percarbonates, the chief source, however, being barium peroxide or sodium peroxide.

The barium peroxide for this purpose is prepared by heating barium nitrate to 300° C. in a current of air. The product is slaked before being dissolved (in hydrochloric acid), its bulk being increased by this treatment, which causes it to crumble down to fine powder. To prepare hydrogen peroxide an earthenware vessel is charged with 20 galls. of water, $3\frac{1}{8}$ lb. of hydrochloric acid and 88 lb. of ice, 7 lb. of barium peroxide being gradually stirred into this dilute acid at 15° C. (59° F.).

When the peroxide has completely dissolved $\frac{3}{4}$ gall. of dilute (40 per cent.) sulphuric acid is added, to throw down the barium as sulphate. The whole is then neutralised with $6\frac{5}{8}$ lb. of sodium phosphate—iron oxide and alumina being thrown down—and finally made alkaline with ammonia before filtering. To neutralise any excess of the alkali the filtrate is run into sufficient dilute sulphuric acid to give a neutral reaction to the liquid, which contains 10-12 per cent. of hydrogen peroxide by volume.

The preparation of hydrogen peroxide from barium peroxide and hydrofluoric acid can be carried out in the following manner:—

Sixteen galls. of water are placed in a wooden vat along with 30 lb. of hydrofluoric acid, and into this mixture is gradually stirred about 30 lb. of barium peroxide previously thinned down to a uniform pulp with 4 galls. of cold water. On adding the pulp to the acid liquor the latter is vigorously stirred with a wooden crutch; and not more than 2 lb. of the pulp should be added at a time, since a larger quantity or insufficient crutching will result in an undesirable rise of temperature attended with considerable loss of hydrogen peroxide.

Commercial barium peroxide and hydrofluoric acid vary in percentage strength. The above quantities refer to concentrated fuming hydrofluoric acid and 85-90 per cent. barium peroxide.

Usually the addition of the barium peroxide pulp to the dilute hydrofluoric acid is continued until, after ten to fifteen minutes' energetic stirring, the solution turns red litmus paper blue. Insoluble barium fluoride and hydrogen peroxide are formed at once; the larger the amount of the latter produced the more gradual the displacement; and to ensure this being complete, the mixture must always be stirred thoroughly. As soon as the above reaction occurs dilute hydrofluoric acid is added until the liquid is again acid to test paper, stirring being then continued vigorously for half an hour, and the mixture left to stand for twelve hours. The barium fluoride settles down and the clear solution of hydrogen peroxide—of about 10-12 per cent. (vol.) strength—is drawn off. The deposited barium fluoride is drained on a filter and thrown into sulphuric acid, to recover the hydrofluoric acid, which can then be used over again.

As already mentioned, sodium peroxide dissolves in cold dilute sulphuric acid without liberation of oxygen, a mixture of hydrogen peroxide solution and sodium sulphate being formed:

$$\underset{\text{Sodium peroxide}}{Na_2O_2} + \underset{\text{Sulphuric acid}}{H_2SO_4} = \underset{\text{Sodium sulphate}}{Na_2SO_4} + \underset{\text{Hydrogen peroxide}}{H_2O_2}.$$

The mixture contains 30 per cent. of hydrogen peroxide by weight.—

Crystalline Hydrogen Peroxide.—The aforesaid crystalline hydrogen peroxide was prepared by W. Staedel from strong solutions—containing up to 95 or 96 per cent. of hydrogen peroxide—though it is said that weaker solutions (80-90 per cent.) will also furnish the crystalline product. The melting point of this latter has been determined as - 2° C. Repeated analyses of Staedel's crystals gave 100 per cent. of hydrogen peroxide, *i.e.*, the product is perfectly anhydrous.

Properties of Hydrogen Peroxide Solutions.—Hydrogen peroxide is a colourless, syrupy liquid which evaporates in the air; it will keep for a considerable time as a slightly acid solution.

The commercial solutions of hydrogen peroxide usually contain about 3 per cent. of H_2O_2 by weight, corresponding to 10-12 per cent. by volume. In addition to a slight excess of phosphoric acid they generally contain a small amount of sodium sulphate and a little magnesium chloride or sodium chloride.

The addition of phosphoric acid and salt improves the keeping qualities of the solution, on which account it has been the custom in practice to sour the bleaching liquor with phosphoric acid in the event of any noticeable decomposition taking place.

The strength of technical hydrogen peroxide solutions is generally expressed by the volume of oxygen that can be liberated per unit volume of solution, the usual 12 per cent. (vol.) of oxygen corresponding to about 3 per cent. of hydrogen peroxide, as stated above.

Stability.—Hydrogen peroxide keeps best at low temperatures, in the dark, and in presence of small quantities of acid. The stability is also improved by the addition of 1 grm. of naphthalene, or 20 grms. of alcohol or ether, per litre.

In presence of alkalis and when heated hydrogen peroxide readily parts with its oxygen ($H_2O_2 = H_2O + O$).

Commercial Hydrogen Peroxide Solutions.—Among the commercial solutions of hydrogen peroxide special mention is deserved by that put on the market by E. Merck of Darmstadt, this preparation being entirely free from acids, salts or organic compounds of any kind. It is sold under the Trade Mark "Perhydrol," and is a chemically pure aqueous solution.

Since the percentage content, by volume, of this preparation

(30 per cent. hydrogen peroxide) corresponds to more than three times the percentage by weight, Perhydrol may be regarded as 100 per cent. pure.

E. de Haën, Hanover, also supplies a solution of hydrogen peroxide, containing over 30 per cent. by weight.

Perhydrol is a water-white liquid, of sp. gr. 1·111 at 15° C. and particularly active. Diluted with distilled water in the proportion of 9 to 1, it corresponds to a 3 per cent. solution of peroxide.

Another preparation, containing up to 65 per cent. by volume, is put on the market by Königswater and Ebell, Linden (Hanover).

Decomposition of Hydrogen Peroxide.—As already mentioned, hydrogen peroxide readily decomposes in water, with liberation of nascent oxygen, on which account it must be classed among the most powerful oxidising agents known. It decomposes, and therefore bleaches, a number of natural and artificial colouring matters.

The decomposition of hydrogen peroxide may proceed suddenly, especially in presence of finely divided solid substances, and thus give rise to violent explosions. In order to prevent this it is usual in practice to employ dilute aqueous solutions only. Contaminated solutions of hydrogen peroxide are liable to result in bleaching failures, owing to the rapid decomposition of the solution, with liberation of oxygen. This decomposition may also occur when the peroxide has been stored for some time, so that the liquid is eventually nothing but ordinary water and not a solution of peroxide at all. When the storage vessel is closed too tightly the pressure of the oxygen disengaged during prolonged storage may burst the vessel, especially when the preparation is not pure.

Purity of Hydrogen Peroxide.—To obtain perfect bleaching it is essential that the hydrogen peroxide preparation used should be quite pure. When, for example, alum and magnesium sulphate have been used in the preparation, the fibres of the fabric to be treated are liable to become clogged with impurities, and therefore will not bleach. Such impure preparations, however, are now rare.

Storage Vessels.—Metals, iron nails or rust, all of which exert a catalytic action on hydrogen peroxide and decompose it at once into oxygen and water, must be avoided. Consequently metal vessels must not on any account be used for storing hydrogen peroxide solutions. Wooden vessels are suitable, but must not contain any iron nails. Earthenware vessels and the like may also be used.

Care in Handling.—Since hydrogen peroxide causes white patches on the skin, care is necessary in handling this substance.

Instability of Hydrogen Peroxide Solutions.—Recent experiments carried on by A. Fischer, on the liability of hydrogen peroxide solutions to decomposition, show that Merck's Perhydrol (30 per cent. hydrogen peroxide) will keep for an unlimited time if carefully stored, though the dilute solutions prepared therefrom with the aid of distilled water will not do so. Solutions of 4-7 per cent. strength decompose more rapidly than such as are either stronger or weaker. From 10 per cent. upwards the stability increases with the concentration. Dilute officinal acids: sulphuric acid, hydrochloric acid and phosphoric acid, in quantities as small as 0·1-0·3 per cent., will considerably retard the decomposition of dilute solutions of hydrogen peroxide; and boric acid also acts as a preservative, though in a lesser degree.

Oxalic acid will not decompose dilute solutions of peroxide at all; and in proportions of 0·1-0·3 per cent., and even up to 2 per cent., it retards decomposition considerably. As already mentioned, it is advisable to dilute the 30 per cent. preparation (or commercial solution of similar strength) to the requisite degree just before use.

Reagent for Hydrogen Peroxide.—Titanium sulphate is found to be the most delicate reagent for hydrogen peroxide, since it will detect the presence of 1 part in 1,800,000 parts of water. When the proportion reaches 1 : 18,000 the reagent turns dark yellow; with 1 : 180,000 it becomes pale yellow, and a pale yellowish tinge is apparent with 1 : 1,800,000.

Valuing Hydrogen Peroxide Solutions.—The value of commercial hydrogen peroxide solutions depends on the content of hydrogen peroxide, the amount of residue, and the presence of free mineral acids, especially sulphuric acid.

The presence of hydrochloric acid and sulphuric acid is first determined qualitatively by means of silver nitrate and barium chloride respectively. Hydrochloric acid gives a curdy, white precipitate with silver nitrate, whilst the presence of sulphuric acid is revealed by the formation of a dense white precipitate (barium sulphate) with barium chloride.

Testing Hydrogen Peroxide.—The hydrogen peroxide content of the commercial preparation can be determined by the following method, devised by W. Dulière: A solution is prepared by dissolving 5·648 grms. of potassium permanganate in 1,000 c.c. of water. This solution is just decomposed by a quantity of hydrogen peroxide solution exactly corresponding to 1,000 c.c. of oxygen.

For testing the commercial preparation 1 c.c. of the latter is measured out, mixed with 30 c.c. of dilute sulphuric acid, and carefully titrated with one drop at a time of the above permanganate solution, until a pink coloration is obtained. Each c.c. of permanganate solution consumed corresponds to 1 c.c. of free oxygen.

The hydrogen peroxide content can also be determined by the following method: The hydrogen peroxide solution is diluted with water until it contains 0·05-0·20 per cent. by weight; and 25-10 c.c. of this solution are then rendered alkaline by the addition of about 5 c.c. of 15 per cent. caustic soda or potash. Twenty-five c.c. of decinormal iodine solution are next added, the nearly colourless liquid being gently inverted several times to disengage the oxygen. The mixture is now acidified with about 10 c.c. of dilute hydrochloric acid (1:1) and the unconsumed iodine is titrated back with decinormal thiosulphate, with or without the addition of starch solution as indicator. (1 c.c. of decinormal iodine corresponds to 0·0017 grm. of H_2O_2.)

Bleaching Wool with Hydrogen Peroxide.—When wool is treated with a commercial (3 per cent.) solution of hydrogen peroxide, that has been diluted with 8 volumes of water and rendered slightly alkaline with a little ammonia (see above), it will not appear to be sufficiently bleached by the first (short) treatment. Nevertheless, by leaving the wool in the bath for about six hours, with repeated turning, and then allowing the material to remain exposed to the air for some time in a damp condition, followed by washing and a short treatment with a strong solution (8-18° Bé.) of sodium bisulphite, succeeded by exposure to the air for twenty-four hours, souring with dilute sulphuric acid (1° Bé.) and repeated washing, the wool will become perfectly white.

Wool and other animal fibres (hair) can be bleached as follows, without requiring any after treatment with bisulphite:—

The wool or hair is first scoured by prolonged treatment with soap solution at 122° F., and is then rinsed.

To prepare the bleaching bath 1-5 galls. of 10-15 per cent. (vol.) hydrogen peroxide solution and 2½ lb. of ammonia (sp. gr. 0·985) are added to each 10 galls. of water (which must be free from lime). The temperature of the bath should be about 68° F.

The dry material is now entered, and left in the bleaching liquor for ten hours, after which it is taken out, wrung or squeezed, and transferred, without washing, to a well-ventilated drying room at a temperature of about 59-62° F.

In this process it is advisable to use several weak bleaching baths in succession, the goods being first entered in the weakest and coldest bath, and left there for about two hours, afterwards passing them through a second, third and fourth bath, each of which is fresher and stronger than the previous one. Finally, a perfectly fresh bath is used, and the goods on issuing from this are wrung and dried at about 59-62° F.

According to another process, recommended by C. A. Fawsitt, the wool is first treated with a solution of alkali silicate (2 lb. per 10 galls. of water), wrung, and entered in a bath consisting of 30 galls. of water, 16 galls. of hydrogen peroxide (10 per cent. vol.) and 2½ lb. of sodium silicate (66° Bé.). Here it is left for twenty-four hours at a temperature of 75° F., and is then taken out, wrung and dried, that is to say, hung up to dry, during which operation the hydrogen peroxide completes its bleaching action.

An analogous bleaching process, in which, however, the goods are subjected to a preliminary treatment with soap solution and an after treatment with oxalic acid, is the following:—

1. *Preliminary Treatment.*—The wool is left for some considerable time in a soap solution at 122° F.

2. *Bleaching Bath.*—After a thorough washing in water, the wool is immersed in a very dilute solution of sodium silicate, until thoroughly soaked. It is next transferred direct into a bleaching bath consisting of 1 part of hydrogen peroxide solution (10-12 per cent. vol.) to 2 parts of pure water, and rendered alkaline to red litmus paper by sodium silicate. The bleaching process is conducted at 100-104° F., and takes one to two hours, the bath being tested at intervals with red litmus paper and treated with an addition of sodium silicate if found no longer alkaline.

3. *After Treatment.*—The bleached wool is rinsed with water, and is placed for a short time in a ½ per cent. solution of oxalic acid, containing a little methyl violet; after which it is rinsed and dried.

It will be evident from the foregoing descriptions that the bleaching bath always contains caustic alkali, which instigates the bleaching action. This latter may, however, easily become too energetic, to avoid which Wolffenstein retards the decomposition of the peroxide by adding weaker alkalis, that just give a basic reaction with litmus. Such compounds include sodium acetate and the salts of several polybasic organic acids.

The process is carried out by treating a 3 per cent. solution of hydrogen peroxide with 10 per cent. of sodium acetate, and allowing this liquor to act on the wool for twenty-four hours. At the end of this time the wool will be completely bleached, whilst only a small quantity of hydrogen peroxide has been decomposed.

Bleaching Silk with Hydrogen Peroxide.—The silk is first scoured with soap and a little soda in the usual manner, followed by souring in slightly acidified water and rinsing in clean water.

To facilitate the uniform moistening of the fibres it is also advisable to subject them, before bleaching, to the action of a 3 per cent. solution of ammonium carbonate, and then immersing the moistened silk in the bleaching bath.

The bleaching liquor is prepared by diluting the 3·2 per cent. solution of hydrogen peroxide with four times its volume of pure water, a suitable quantity of magnesia being added. After twenty-four hours the silk is taken out, and when washed and dried will be bleached sufficiently white but deprived of part of its lustre, and will have acquired a rough texture. The fibre, however, is not weakened.

In a further experiment the scoured silk was treated with hydrogen peroxide solution diluted with 4-6 volumes of water and a little ammonia, and then put through an after treatment with sodium bisulphite solution (15 ° Bé.) containing a little hydrochloric acid. This gave a fully bleached product that retained its lustre and smoothness.

A similar result was obtained by entering the silk, after twelve hours' immersion in the bisulphite liquor, in a bath of very dilute hydrochloric acid, followed by washing and drying. The results of a number of trials showed that strong bleaching baths are required for bleaching silk with hydrogen peroxide.

The use of magnesia causing the silk to feel rough, it seems advisable to remove any magnesia adhering to the fibre by means of dilute hydrochloric or sulphuric acid. When magnesia is used, the hydrogen peroxide liquor may also be warmed.

In the experiments mentioned above, the bleaching liquors were not warmed.

Silk can be well bleached without suffering any loss of gloss, strength or elasticity by the sufficiently prolonged action of a hydrogen peroxide bleaching liquor of suitable strength (rendered alkaline by a little ammonia), followed by an after treatment with sodium bisulphite solution, preferably succeeded by a short immersion in dilute hydrochloric acid.

The goods are preferably left in the bleaching bath, with frequent turning, until the desired effect is obtained. In many instances, however, it is sufficient to impregnate the material with the bleaching liquor, and squeeze out the surplus, the material being then left exposed to the air for a considerable time, and treated over again if necessary.

C. A. Fawsitt recommends, for bleaching silk, a mixture of 10 galls. of hydrogen peroxide solution (10 per cent. vol.) and 20 galls. of water, containing 4 oz. of caustic soda and 6 oz. of sodium silicate.

Ammonia, magnesium sulphate and caustic soda may all be replaced by sodium silicate. For each 10 parts, by weight, of scoured and rinsed silk, the bleaching bath is charged with 5-15 parts of hydrogen peroxide (10-12 per cent. vol.) according to the quality of the goods—chappe silk, for instance, requiring a much smaller quantity of bleaching agent than tussah silk. The acidity of the hydrogen peroxide is neutralised with sodium silicate to produce the necessary alkaline reaction, 1 part of sodium silicate solution being added for every 10 parts of hydrogen peroxide.

In this bath the bleaching of chappe silk may be carried on at a temperature of 150-165° F.; whilst in bleaching tussah silk the bath must finally be heated to 212° F. As a rule the goods will be found sufficiently bleached after being worked about for a few hours in the bath. An immediate rinsing follows; and it is also advisable to treat the bleached goods in a soap bath, a trace of methyl violet, etc., being added.

If it be desired to impart "scroop" to the silk the latter must be passed through a liquor containing acetic acid.

According to the process of L. J. Mathos, the cocoons of tussah silk are first softened in warm water, and then treated with a seventy-five fold quantity of carbonate of soda solution, containing 8-10 per cent. of carbonate, based on the weight of the silk. The cocoons are then unwound and the silk is wrung. In this treatment the silk loses about 10 per cent. of its original dry weight. The actual scouring of tussah silk is performed in a 25 per cent. solution of carbonate of soda, the alkalinity being then neutralised with dilute hydrochloric acid, followed by a thorough washing. The bleaching can be effected with the above solution of hydrogen peroxide. Mathos recommends an after treatment with potassium chlorate and sodium nitrite.

According to another process, the natural brown tussah silk is wetted in a lukewarm 1 per cent. solution of carbonate of soda, followed by immersion for two hours in a soap solution containing 10-12 per cent. of soft soap (based on the weight of the silk). The scoured silk is still of a brownish colour, though for many purposes this is no drawback. The bast soap from the scouring process cannot be used over again, and must therefore be thrown away. To reduce the colour of the silk to a light shade or white it must be entered for ten hours in a strong solution of hydrogen peroxide, containing a little borax, at 158° F., followed by a boiling hot 5 per cent. soap bath and then by a lukewarm bath of soap.

A new process for bleaching silk consists of adding glycerine, an alcohol, a ketone or an aldehyde to the hydrogen peroxide solution, this addition being said to render the scouring of the silk unnecessary. For example, 22 parts by weight of raw silk are heated for an hour in a vessel charged with 22 parts of a 3 per cent. solution of hydrogen peroxide and 22 parts of acetone, the vessel being fitted with a reflux condenser. Again, 11 parts of boiled chappe silk are treated for twenty-four to forty-eight hours in the cold with 33 parts of hydrogen peroxide solution and 22 parts of alcohol. In both cases the addition of a little ammonia is advisable.

Bluing before Bleaching.—It is worthy of mention in this place that in bleaching animal fibres with hydrogen peroxide the process is frequently supplemented by slightly bluing the fibres, which otherwise are not bleached perfectly white. According to the patented process of the Chémische Fabrik Opladen, the wool or silk to be bleached may be blued beforehand, by treating it with a dilute solution of some bluish dye, such as Acid Violet, Alkali Blue, or the like, until it has acquired a faint bluish tinge. The usual bleaching treatment is applied afterwards. This procedure is claimed to effect a considerable saving of hydrogen peroxide, in addition to furnishing a pure white.

Bleaching Cotton with Hydrogen Peroxide.—Cotton is usually bleached with bleaching powder, an agent that cannot be replaced by the much dearer hydrogen peroxide. Nevertheless the latter is sometimes used for treating certain classes of cotton goods, such as fine counts of yarn. A perfect, full bleach can be obtained by combined treatment with hydrogen peroxide and bleaching soda. The goods are first treated with carbonate of soda solution, then with dilute caustic soda (10 parts of caustic soda, sp. gr. 1·16, to 100 parts of water), in a bowking kier, for about six to eight hours, in the usual manner, and afterwards suitably rinsed and squeezed. After this preparatory treatment the goods are put through a souring bath (sp. gr. 1·03), transferred to a bath of bleaching soda (sp. gr. 1·005), and left in a heap for one hour. After a good washing the goods are passed through caustic soda (sp. gr. 1·07), washed again and put through a wringer. They are next entered in the hydrogen peroxide bath, which has been prepared by diluting 2¼ galls. of commercial hydrogen peroxide with eight times that quantity of water, 8 oz. of ammonia (20° Bé.) being added. In this liquor the goods are left for at least eight hours (*i.e.*, until perfectly white) at a temperature of about 77-86° F., and are afterwards put through a wringer and dried in the air (exposed to the light.)

Bleaching Linens with Hydrogen Peroxide.—According to Ubicini, grass bleaching may be replaced by hydrogen peroxide; but the latter is more expensive.

Hydrogen peroxide bleaching is not equal in all respects to grassing, the action of which latter process, according to Ubicini, is partly due to the ozone present in the air. The serial order of the operations in the Ubicini process is as follows: Soaking the goods, washing, liming (2-3 per cent.), souring with hydrochloric acid, washing in a 2 per cent. bath of carbonate of soda, 1 per cent. of caustic soda, 0 5 per cent. of resin, soaping for three hours at 122° F., washing for three hours, and treating with hydrogen peroxide at 120-140° F., the goods being turned at frequent intervals. A treatment with hydrochloric acid completes the process.

Bleaching Jute with Hydrogen Peroxide.—Jute always requires to be cleansed before bleaching, by boiling it in a 5 per cent. solution of carbonate of soda, followed by rinsing.

The bleaching of jute (Chinese and East Indian fibre, or jute fabrics) is effected with a 10-12 per cent. (vol.) solution of hydrogen peroxide, containing 2 per cent. of ammonia (20° Bé.). The jute must be left in this bath for one to two days at a temperature of 77-86° F. After being taken out the goods are dried in the air.

The cleaned material can also be dipped in the above bleaching bath and properly steeped, the surplus liquor being then expressed in a wringer, and the still damp material dried slowly at 68° F. This latter operation must be repeated if a successful result is desired.

With commercial hydrogen peroxide solution, diluted with an eight-fold quantity of water and made slightly alkaline with ammonia, the jute will not be sufficiently bleached, even by two days' immersion in the bath; and it is only by repeating the treatment for the same length of time, and supplementing it with an after treatment with sodium bisulphite, that a nearly pure white can be obtained.

As previously mentioned, jute (and especially fine yarn) can be bleached by the permanganate process. After a suitable treatment with carbonate of soda and permanganate solution the goods are worked about in dilute hydrochloric acid containing hydrogen peroxide solution, and then washed. The process must, however, be repeated in order to obtain a perfect white. In a recent process, patented by Martin, the jute is first of all boiled in an autoclave for four hours, in a solution containing, for 12 cwt. of material, 1 cwt. of calcined soda, 6 lb. of oil of turpentine and 6 lb. of carbon disulphide. In this process an attempt is made to reduce the consumption of the bleaching agent to one-half.

Bleaching Various Vegetable Fibres with Hydrogen Peroxide.—Manila hemp can be bleached with hydrogen peroxide in the same way as jute. With this object the commercial hydrogen peroxide (3·2 per cent.) is diluted with only five to six times its volume of water, the liquid being rendered alkaline with about 2 per cent. of ammonia. The Manila hemp is soaked in this bath for one to two days, and if not then sufficiently bleached is subjected to a repetition of the same treatment. The goods are then taken out, wrung and placed for a short time in a dilute solution of sodium bisulphite, followed by suitable washing and drying. In this process the lustre and strength of the fibre are preserved.

The various kinds of hemp behave somewhat differently under the action of hydrogen peroxide. Before bleaching they must be cleansed by a faintly alkaline agent; and the bleaching liquor may be prepared by diluting hydrogen peroxide solution with 4 volumes of water, a little ammonia being added to produce an alkaline reaction. In the case of Prussian or Russian hemp the material is left in the bleaching liquor for three to four days, whereas Italian hemp will be sufficiently bleached in about one and a half days. After leaving the bath the material is slightly rinsed, wrung and hung up to dry while still damp, preferably in the air.

Sisal hemp (Pita fibre) can be bleached, in accordance with its practical application, by an alkaline hydrogen peroxide liquor (1 : 4), the operation being repeated when the hemp is required as weft for upholstery fabrics. Mexican fibre may be bleached in the same way as Sisal.

New Zealand hemp is bleached with a similar, slightly alkaline hydrogen peroxide liquor, by immersion for about three days. This will make the fibres a nearly pure white, sufficiently so for the purposes for which they are intended, and they may then be taken out, rinsed, wrung and hung up to dry, preferably in the air. The lustre of the fibres is unimpaired.

Bleaching Straw, Wood, etc., with Hydrogen Peroxide.—For bleaching straw the following bleaching liquor is used: Commercial hydrogen peroxide (3·2 per cent.) is diluted with twice its volume of pure water, and treated with 4 oz. of sodium silicate to every 6 galls. The silicate may be replaced by ammonia (sp. gr. 0·910), at the rate of 1 lb. per 10 galls. A bath of this kind can also be used for bleaching wood (plates, ornaments), the material being immersed for about five days at a temperature of about 65-68° F. A little fresh ammonia (about 1½-2 oz.) is added to the bath at intervals of about eight hours. After removal from the bath the material is bleached slowly at a low temperature.

The colouring matters and extractives deposited in the cells of the material are completely eliminated by this process.

Bleaching Feathers with Hydrogen Peroxide.—Feathers must be thoroughly cleansed with petroleum spirit or soap solution, before bleaching, to remove both the natural fat and all traces of accidental grease from external sources. With this object the feathers are soaked for six to eight hours in petroleum spirit in a closed vessel (to prevent loss by evaporation). If possible, each separate feather should be moved about gently, in order to facilitate the extraction of the fat; but violent agitation must be avoided, owing to the risk of tangling the feathers. When cleansed, the feathers are dried in a moderately strong current of warm air. While they are cooling, the bleaching liquor is prepared, cooling being found to be indispensable to the attainment of a full bleach.

According to another process the feathers (ostrich feathers) are cleansed in the usual way by washing in a warm solution of soap, freed from grease with very dilute ammonia, and then entered into the bleaching bath.

Worn and tangled feathers have to go through a preparatory treatment. For this purpose 4 oz. of white tallow soap are dissolved, by boiling, in about 1 gall. of soft water, the solution being skimmed and set aside to cool. In the meantime the feathers have been soaked in lukewarm water, and are next washed with the cold soap solution, preferably by spreading them out on a smooth, clean support, the soap solution being applied with a pad of linen cloth. The washed material is rinsed with lukewarm water, then laid between two clean, dry linen cloths and patted gently with the hand. When nearly dry the feathers must be taken out of the cloths, and curled and dried by the heat of a coke fire, which must be smokeless.

The bleaching liquor consists of undiluted hydrogen peroxide solution (10 per cent. vol.), to which has been added just sufficient ammonia to leave it faintly acid to litmus paper. During the bleaching process the feathers must naturally be completely submerged and protected from light. The operation takes from eight hours to three days. The remarkable difference in the time is due to differences of origin and age of the feathers, and the adherent natural colouring matters. During the first part of the process the goods are gently moved to and fro in the bath. When the desired degree of bleaching is attained the feathers are rinsed in soft water, preferably rain water. Rinsing is followed by a bath of spirit, containing 10 per cent. of ether, this being succeeded by another rinsing, draining in the hydro-extractor and drying.

When dry the feathers are passed three or four times through pure benzine, and waved about in the air until dry. Curling is done with a knife.

Instead of the foregoing process, which, however, yields results that satisfy all requirements, the feathers may, as already mentioned, be first treated with a warm solution of soap, followed by very weak ammonia, and then placed in a hydrogen peroxide solution (10 per cent. vol.) that has been made very faintly alkaline with ammonia, the temperature of the bath being about 85-95° F. About 11 lb. of the cleansed material can be bleached with 2¼ galls. of liquor, the feathers being kept in the bath for about twenty-four hours and worked about frequently. On removal from the bath the bleached feathers are rinsed with cold water, and then laid for about two hours in a cold solution of crystallised tartaric acid (2½ per cent. strength). This is followed by rinsing with cold water until the acid reaction has completely disappeared, after which the feathers are dried.

C. A. Fawsitt recommends that the bleached and washed feathers should be passed through a bath of very dilute sulphuric acid to stiffen the quills.

Bleaching Leather with Hydrogen Peroxide.—As is well known, tanned leather contains a considerable amount of tannin and grease. Chamoy leather, which is prepared by an oil process, must be freed from impurities and fatty matters before bleaching by washing with soap and water, the soap being removed by repeated and prolonged rinsing with soft water. Bleaching is effected in a hydrogen peroxide solution (10 per cent. vol.) that has been treated with 2¼ per cent. of ammonia (20° Bé.), the bath being warmed to about 85-90° F. The leather is left in the bath for about twenty-four hours, with frequent turning. When bleached the material is well squeezed, and then washed for a long time in soft water, followed by slow drying in a current of air, being worked about frequently. Catgut and horn may also be bleached by the same process; but with regard to the latter another method will be given later on.

According to Borntrager tanned leather (also chamoy leather) is digested for an hour at 104° F. with benzine (to remove fat, etc.), drained, the surplus solvent being removed by warming the leather in the water bath, after which the material is bleached in hydrogen peroxide solution, made alkaline with ammonia. When bleached the leather is squeezed and washed, and then dried slowly in the air, as mentioned above. This process gives an excellent product, of a pale reddish white colour.

Leather may also be bleached by a process analogous to grassing. The bleaching liquor is a very faintly alkaline solution of hydrogen peroxide (10 per cent. vol.), prepared by dropping ammonia slowly into the stirred peroxide solution until it begins to turn red litmus paper blue. The material is entered in this bath for some time, then squeezed, and hung up to dry slowly in a current of air. The whole process is generally repeated twice, the bleached leather being finally dried slowly in a draught, and repeatedly worked about the while.

Bleaching Ivory, Horn, Bones and Similar Articles.—Ivory may be bleached in hydrogen peroxide (10 per cent. vol.), diluted with twice its volume of distilled water, sufficient ammonia being added to make the liquor neutral to both red and blue litmus paper (or at any rate very slightly acid), no preliminary treatment being required. Bones must be freed from fat, etc., before bleaching, benzine, ether or a solution of carbonate of soda being used. Borntrager recommends the following process for bleaching ivory, horn and bones:—

An ethereal liquor is prepared by shaking up hydrogen peroxide with ether or benzine, so as to dissolve the former. The mixture is separated in a separating funnel, and the solution (which contains about 50 per cent. of oxygen by volume) is used for treating ivory, horn, etc., the fat being dissolved and extracted, and the material bleached at the same time.

This process, being very expensive, is restricted to the treatment of fine goods. The bath already recommended for ivory can be used for bleaching bone or horn that has been freed from fat with carbonate of soda solution. The materials must remain in the bath for about twenty-four hours, at a temperature of about 85-95° F., and be then transferred for about fifteen hours to a similar bath, the temperature of which is only 68° F.

After removal from the bath the materials are dried slowly in the air, exposed to the light (preferably direct sunlight).

Bleaching Hair.—Human and animal hair must be sorted and thoroughly cleansed before bleaching. For this purpose the hair is thoroughly washed with soap and warm, soft water, and then immersed in dilute ammonia until it no longer repels water. The bleaching liquor is hydrogen peroxide solution (10 per cent. vol.) containing $2\frac{1}{4}$ per cent. of ammonia; and in this the cleansed material is left for about twenty-four hours at a temperature of 86° F. The operation does not proceed uniformly, owing to differences in the composition of the colouring matter, which is more or less altered and rendered soluble by the action of the hydrogen peroxide; so that some kinds of hair turn yellow and then white (occasionally with a yellowish or bluish tinge), whilst others are very difficult to bleach at all. Usually a second, fresh bath is necessary in order to bleach the material sufficiently. When the operation has been carried far enough the hair is squeezed, placed in pure, soft water, containing 1/100 per cent. of concentrated sulphuric acid (66° Bé.), and weighted down in this liquor for a long time. It is then washed repeatedly with pure water and dried in the air. Bleached and washed human hair must be dipped, while still moist, in a solution of spirit, containing a little oil and glycerine, and then gradually dried in a draught.

Cleansed animal hair can generally be bleached by the following treatment: 1 part of commercial hydrogen peroxide solution (10 per cent. vol.) is diluted with an equal quantity of soft water and treated with 1½ per cent. of ammonia, the hair being left in this bath for twelve hours at 68° F. The material is then taken out, squeezed and dried, without washing, in a well-ventilated and lighted room warmed to about 60-63° F. It is advisable, however, to use a series of weaker baths, the material being entered first in the weakest and coolest liquor (*e.g.*, 1 part of hydrogen peroxide and 5 parts of water), and then in a second, third and fourth bath, each freshly prepared and stronger than the preceding one. Finally the material is treated in a fresh bath containing equal quantities of peroxide solution and soft water. On removal from this bath the hair is squeezed, and is then dried as described above.

Bleaching Sponges with Hydrogen Peroxide.—Since sponges contain calcium carbonate and iron oxide these constituents must be removed, before bleaching, by means of dilute hydrochloric acid. For this purpose it is generally sufficient to treat the sponges with a mixture of 5 parts of technically pure hydrochloric acid (21° Bé.) and 100 parts of water, for eighteen to twenty-four hours; though in some cases the operation must be repeated. When the sponges are stained in red patches, a mixture of 20 parts of pure hydrochloric acid and 100 parts of water must be used for the preparatory treatment. After the above-named compounds have been dissolved out by the acid the sponges are squeezed by powerful pressure, and washed thoroughly in clean water, to remove the acid completely.

The cleansed sponges are bleached in commercial hydrogen peroxide solution (10 per cent. vol.) containing 2¼ per cent. of ammonia (20° Bé.), pressed down with wood or glass, and left in the bath for two to three days (according to the quality of the sponges) at a temperature of about 68° F., during which time they should be worked about and pressed repeatedly. When finished they are taken out, squeezed and slowly dried in a draught, preferably in sunlight.

CHAPTER IX.

NEW PROCESSES AND AGENTS FOR BLEACHING FATS, OILS, WAX, PARAFFIN, SOAP AND GLUE.

A. BLEACHING FATS, OILS, WAX AND PARAFFIN.

New Process for Bleaching Fats and Oils.—H. A. Metz and P. S. Clarkson have devised a new process for bleaching fats and oils, based on the action of hydrosulphites, or of hydrosulphite-formaldehydes and sulphoxylates.

(*a*) Maize oil (200 parts) is mixed with cold water (200 parts) containing sodium hydrosulphite (15 parts), the last-named substance being prepared by means of zinc dust and sodium bisulphite. The mixture is placed in a closed vessel for about ten hours, stirred at intervals and then left to settle. At the end of several hours the amber colour of the oil will have changed to pale straw yellow, and after a further thirty-two hours will be quite colourless.

(*b*) Seed oil (200 parts) is mixed with cold water (600 parts) containing 10 parts of hyraldite NF (*q.v.*), or an equivalent quantity of a similar substance, in which a combination of sodium hydrosulphite and formaldehyde forms the active ingredient. The mixture is stirred up well in a closed vessel and warmed to 158° F. When cool the liquid is treated as described above.

(*c*) Raw linseed oil (200 parts) is mixed with cold water (400 parts) containing sodium hydrosulphite (20 parts). After stirring thoroughly in a closed vessel the mixture is left to settle for thirty-two hours, by which time the oil will have been decolorised to a considerable extent, without having sustained any alteration. The upper layers of bleached oil are syphoned off, and the remainder is extracted with petroleum spirit; or the whole of the oil is recovered by means of a solvent, which is expelled by distillation.

Bleaching Wax.—E. Weingärtner employs for bleaching beeswax, carnauba wax, etc., aluminium-magnesium hydrosilicate (fuller's earth), which has long been used for decolorising oils, his procedure being as follows:—

One hundred parts of crude beeswax are heated, with constant stirring, to about 266° F., 10 parts of fuller's earth being then added in small quantities, and the temperature raised to 300-338° F., though not higher. During the heating process the fuller's earth absorbs the colouring matters of the wax, and becomes dark coloured and finally black in the process, whilst the colour of the bleached wax gradually changes from yellow to white. From time to time small samples of the wax are taken, these being filtered and set to cool on a glass plate, in order to see whether the bleaching is complete. As a rule bleaching will be finished in thirty minutes, whereupon the application of heat is suspended, and the warm wax is separated from the fuller's earth by filter presses, centrifugal machines, or the like. The residue, which still contains about 50-60 per cent. of wax in addition to the fuller's earth and impurities, is extracted with carbon tetrachloride, carbon disulphide, or the like, in order to recover the wax.

Bleaching Paraffin Wax.—Bavarian and Silesian fuller's earth can be applied to bleaching paraffin wax, in addition to the bleaching of fats and oils.

B. BLEACHING SOAP.

Decrolin and Blankite for Bleaching Soap.—The Badische Anilin & Sodafabrik has put on the market two bleaching agents for soap, "Decrolin" and "Blankite". The former of these is a soluble greenish powder for bleaching soft soaps, and is prepared by the reduction of salts of formaldehyde-sulphurous acid, $CH_2O . H_2SO_3$. (Ger. Pat. 165,807.)

Decrolin is a powerful reducing agent, its bleaching action being only exerted at high temperatures, so that it must be dissolved in hot water, and the solution added to the soap towards the end of the boiling process. About ¼ per cent., based on the weight of the finished soap, is sufficient for bleaching. The best effects are produced on soaps for which whiteness is of more importance than transparency.

Blankite (pure, anhydrous sodium hydrosulphite, $Na_2S_2O_4$) is a fine, white powder, soluble in water, and is used for bleaching curd soaps. For this purpose 1 part of Blankite is dissolved in 10 parts of cold water, a small quantity (about 2 fluid oz. per 1 lb. of Blankite) of caustic soda lye being added, and the mixture crutched into the boiling soap before the separation of the curd. Another method is to strew the fine powder over the boiling soap paste. Thorough stirring is necessary, to ensure the bleaching agent coming into contact with all parts of the soap. About 0·2-0·3 per cent. of the agent is sufficient. The solution must be used at once, since its power diminishes when kept for some time. The bleaching action is based on energetic absorption of oxygen, the hydrosulphite being converted into bisulphite; or in an alkaline solution, into sodium sulphite and sulphate.

C. Bleaching Glue.

The best agent for bleaching glue is the zinc salt of formaldehyde-sulphoxylic acid, this salt not being liable to the defect of the corresponding sodium salt, which, in presence of metallic salts, undergoes partial decomposition, whereby metallic sulphides are formed and the glue is turned grey.

For carrying out the process the glue is heated, that is to say the glue liquor in the boiling pan is maintained at about the boiling point of water, and the basic zinc salt of formaldehyde-sulphoxylic acid is added in the form of a thin pulp (mixed with water) and well stirred in. The colour becomes lighter within a few minutes. About 4½ lb. of the zinc salt will bleach a ton of glue. The after treatment is of the usual kind. Occasionally an addition of acid to the glue liquor is desirable.

This technically important process forms the subject of a patent by the Badische Co.

CHAPTER X.

SOLID, STABLE CALCIUM HYPOCHLORITE AND BLEACHING SODA.

A. Stable Calcium Hypochlorite.—The Griesheim-Elektron Chemical Co. has patented a process for the manufacture of stable, solid calcium hypochlorite, in which "chloride of lime" solution is evaporated under conditions reducing the risk of decomposition to a minimum, the crystals deposited from the liquor being separated and dried in a suitable manner.

The new "chloride of lime" obtained in this manner possesses the following advantages over the ordinary preparation:—

1. When treated with hydrochloric acid it liberates 80-90 per cent. of its own weight of active chlorine.

2. It is soluble in water, to a colourless and almost perfectly clear solution, so that no special clarifying plant is required by the user and no troublesome waste product is formed.

3. When exposed to the air it does not become soft and greasy (like ordinary bleaching powder), since it contains but little calcium chloride.

4. It is an excellent bleaching agent, since it can be made to liberate free chlorine, free hypochlorous acid or oxygen, as desired.

5. It is of a high degree of purity and easy to work.

B. Bleaching Soda.—There are several ways of making this preparation, one of them consisting in pouring fused caustic soda, in suitable amount, and in small quantities at a time, on to carbonate of soda, and then passing the mixture through a mill. Another method is to boil together sodium silicate, water and ammonia-soda, the mixture being poured into shallow moulds to set. Henkel's bleaching soda consists of: Water 48·56 per cent., gelatinous silica 18·26, sodium silicate 16·59, carbonate of soda 15·76, caustic soda 0·32, sodium chloride 0·39, alumina 0·024 and ferric oxide 0·096 per cent.

Heilpern and Haas' bleaching soda contains: Water 1·685 per cent., gelatinous silica 0·460, carbonate of soda 84·788, caustic soda 0·160, sodium chloride 7·805, sodium sulphate 4·414, alumina 0·520, ferric oxide 0·044 per cent. and traces of calcium carbonate.

CHAPTER XI.

ELECTRIC BLEACHING.

THE electric current is utilised in the preparation of a bleaching agent to replace bleaching powder.

"Electric bleaching" implies bleaching with a substitute for bleaching powder, prepared by an electrical process, but used in the same way as the ordinary preparation. Owing to the numerous drawbacks of ordinary bleaching powder, which drawbacks it was desirable to remove, both on the score of economy, reliability, cleanliness and convenience in working, attempts were made, more than twenty years ago, to replace this substance by some other bleaching agent.

Electrolytic Bleaching Lye.—These attempts resulted in the production of an "electrolytic bleaching lye" analogous in composition to bleaching powder, except that completely soluble sodium compounds were present in place of the lime compounds that always left an insoluble residue.

The most important constituent of bleaching powder is calcium hypochlorite ($Ca(OCl)_2$), in addition to which the compounds Cl-Ca-OCl, calcium hydroxide and calcium chloride, are present, whilst the electrolytic lye, which is a perfectly clear liquid, contains sodium hypochlorite, NaOCl. When bleaching powder is dissolved a residue is left; and on the resulting lye being exposed to the air after careful settling it again becomes turbid from the presence of particles of lime, whereas this is not the case with the lye prepared by the electrolytic process.

The application of the electrolytic preparation is specially advisable when no suitable dissolving apparatus for bleaching powder is available, or the workers are not thoroughly skilled bleachers. When water power or a cheap source of steam is at disposal, and where the formation of injurious effluents must be avoided, the electrolytic process is advisable, especially since, with good apparatus, it is cheaper than the ordinary method. In fact it may be used for all purposes for which bleaching powder is suitable; and is advantageous for bleaching jute, hemp, etc., as well as being applicable to the bleaching of cotton, linen, paper, cellulose, etc. Fine goods, such as lace, curtains, bandages and the like, are usually not bleached with bleaching powder, but with the decomposition product of that agent and carbonate of soda.

Sodium hypochlorite is prepared by treating bleaching powder with carbonate of soda or sodium sulphate, according to the equation: $Ca(ClO)_2 + Na_2CO_3 = 2NaClO + CaCO_3$ (or $Ca(ClO)_2 + Na_2SO_4 = 2NaOCl + CaSO_4$). Wherever it has been the practice to use solutions of sodium (or potassium) hypochlorite, which are also known in commerce as Eau de Javelle, Eau de Larraque, Chlorozone, Bleaching Soda, etc., these liquids can be replaced, for bleaching, by the electrolytic bleaching lye in question.

In preparing these electrolytic bleaching liquors use is made of various salts, including sodium chloride or common salt ($NaCl$), magnesium chloride ($MgCl_2 + 6H_2O$), calcium chloride ($CaCl_2 + 6H_2O$) and carnallite, a double chloride of potash and magnesia ($KCl, MgCl_2, 6H_2O$).

The actual founder of the electrolytic bleaching industry was C. Hermite, who, more than twenty years ago, electrolysed sea water and afterwards dilute solutions of magnesium chloride.

Roscoe and Lund electrolysed sea water in an apparatus devised by Hermite; and it was found that a solution containing 0·1 per cent. of active chlorine lost 10 per cent. of the same in twenty-four hours, the loss with a 7·5 per cent. solution being 34 per cent., and with a 0·05 per cent. solution

90 per cent. of the active chlorine. Hence, the greater the dilution of the bleaching liquor the more rapidly it is decomposed; though the temperature, and above all the degree of alkalinity, of the bleaching liquor influence its stability. Correspondingly diluted solutions of magnesium chloride behave similarly to sea water on electrolysis; but the liquors prepared by the electrolysis of sodium chloride solutions are more stable. The development of the electrical bleaching industry is intimately connected with the progress made in the apparatus employed for making the bleaching liquors.

Though the liquors made by Hermite from sea water and magnesium chloride were not inferior to those now obtained from electrolysed salt solutions, he was unable to carry out his invention successfully, because, in practice, his apparatus exhibited defects which were gradually recognised.

The preparation of electrolytic bleaching lyes necessitates the use of a dynamo, the (continuous) current furnished by this generator being passed through a solution that is usually prepared by dissolving rock salt (sodium chloride) in water, the other chlorides mentioned above being rarely employed. During electrolysis the cathode metal (metal of the negative pole) decomposes the water, with formation of alkali hydrate (caustic soda), whilst chlorine is liberated at the anode (metal of the positive pole). The principal feature of an electric bleaching plant is the electrolyser in which the bleaching liquor is made; and the plant must also contain a vessel for preparing the salt solution, and a tank, made of cement, concrete earthenware, or wood lined with lead, for the reception and storage of the finished liquor. No alteration in an existing plant employing bleaching powder is needed when electric bleaching is introduced, all the addition necessary being the provision of the electrical appliances.

Judging the Utility of Electric Bleaching Plant.—The following points must be considered in judging the utility of an electric bleaching plant:—

1. The consumption of power for a given weight of chlorine in a given time.

This consumption of power, expressed in kilowatt hours, is the product of the amperage of the current, the voltage (measured at the apparatus) and the number of hours occupied. The weight of chlorine produced is ascertained from the volume of the bleaching liquor made and the number of grains of chlorine per gallon.

Example. An apparatus working with 70 amperes at 110 volts produces in ten hours 121 galls. of liquor containing 1,400 grains of active chlorine per gall. The consumption of power is 70 × 110 × 10 ÷ 1000 = 77 kilowatt hours, or 7·7 kilowatts per hour, that is to say about 12 mechanical horse-power during the ten hours; and the weight of chlorine produced is: 121 × 1400 ÷ 7000 = 24¼ lb.

2. The consumption of salt, that is to say the strength of the bleaching liquor.

This factor depends on both the concentration of the solution of salt used and the strength of the resulting bleaching liquor.

Since the volume of the bleaching liquor is identical with that of the original solution taken, the amount of salt consumed in producing 1 gall. of liquor is greater in proportion as the original solution was more concentrated.

Example: If a salt solution be employed containing 1 lb. of salt per gall., this weight of salt is consumed for every gall. of liquor produced, and according to the strength of the liquor in active chlorine, so will the yield from that weight of salt vary, the higher the concentration of the liquor the lower the consumption of salt per unit of chlorine.

Example: If the bleaching liquor contain 1,400 grains of chlorine per gall., 5 lb. of salt have been consumed in producing 1 lb. of chlorine; but if the liquor contain only 840 grains of chlorine per gall. the consumption of salt per 1 lb. of chlorine has been 8·3 lb. Again, if a 15 per cent. solution of salt have been used—containing $1\frac{1}{2}$ lb. of salt per gall.—and the resulting liquor contain only 840 grains of chlorine per gall., then $12\frac{1}{2}$ lb. of salt have been consumed in the production of 1 lb. of chlorine.

3. The concentration of the liquor furnished by the apparatus in its relation to the material to be bleached.

Some materials, cellulose for instance, contain such a quantity of water when they come to be bleached that strong solutions of chlorine alone are suitable, since otherwise the water in the material would dilute the liquor to such an extent as to render it inoperative. For this purpose a solution containing 1,400 grains of active chlorine per gall. (corresponding to chloride of lime solutions of about 5° Bé.) are found to be strong enough for this purpose. If, however, the electrolyser be incapable of furnishing liquors of this strength, and only produces those containing 840-1,050 grains of chlorine per gall., the apparatus will not suit for some of the purposes for which the bleaching liquor may be required.

4. The concentration of the bleaching liquor in view of replenishing the spent bleaching bath.

In chemick bleaching it is a usual practice to regenerate the lye with bleaching powder when it has become so far spent as to have no bleaching effect on freshly introduced material. A similar method may be adopted with electrolytic lye, provided it be of sufficient strength.

5. The durability of the apparatus.

This factor depends to a great extent on the working life of the electrodes, that is to say the parts by which the electric current is introduced into the apparatus. In the present types of electrolytic apparatus these electrodes consist either wholly of carbon (*e.g.*, graphite) or platinum, or of the two together. Apparatus with exclusively carbon electrodes wear away at the positive pole, the positive electrode being corroded in course of time. With platinum negative electrodes there is also risk of wear, owing to the platinum at the negative pole becoming spongy. On the other hand, experience has shown that platinum is durable at the positive pole and carbon at the negative pole. With platinum apparatus mechanical cleaning is essential, though difficult on account of the thinness of the platinum.

6. The capacity of the apparatus at different times.

It sometimes happens that electric bleaching apparatus that has worked well at first loses its efficiency afterwards; and therefore some time must necessarily elapse before a definite opinion can be pronounced on the suitability of any apparatus, or whether it will fulfil the guarantees given.

7. The material value of the apparatus.

The value of the apparatus depends chiefly on the materials used in the electrodes. One with carbon electrodes only has but a small material value, whilst apparatus with platinum electrodes always possesses considerable material value, which remains constant except when the platinum is used at the negative pole.

Other points to be taken into consideration are the accessories, such as pumps and the like.

Owing to the differences in the methods of using and preparing the bleaching agent in the "electric" bleaching processess the latter are divided into three classes; direct, indirect and auxiliary processes. In the direct process the haloid salt (sodium chloride) is electrolysed in the same vessel that is intended for bleaching, the active halogen (chlorine) or the oxygen of the bleaching compound being immediately consumed by the material to be bleached. In the indirect process the bleaching agent is prepared in an electrolyser that is distinct from the bleaching vat, so that the bleaching agent is not immediately employed for oxidising the material. The most important of the indirect processes seems to be that in which a solution of sodium hypochlorite is produced in the electrolyser; and most of the methods applied in practice are based on this process. The other processes cannot be discussed more fully here.

Bleaching Experiment with Electrolysed Sodium Chloride Solution.—The fact that a real bleaching liquor can be obtained by the electrolytic decomposition of a solution of common salt (sodium chloride) can be demonstrated by the following experiment: The cell (Fig. 3) is charged with a 10 per cent. solution of salt and fitted with two carbon plate electrodes, the anode being covered with red calico. After a current from a battery of five accumulators has been allowed to act upon the electrolyte for ten minutes the fabric will be found to have turned quite white.

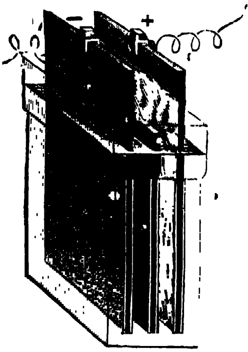

FIG. 3.—Cell charged with 10 per cent. solution of common salt and fitted with two carbon plate electrodes.

Electrolytic Decomposition of Sodium Chloride.—In the electrolytic decomposition of this salt the chloride is separated into its constituent elements, sodium and chlorine, the former (in so far as it is isolated at the cathode) combining with water to form sodium hydroxide (caustic soda) and hydrogen, according to the equation: $Na_2 + 2H_2O = 2NaOH + H_2$. This reaction explains why no deposition of metallic sodium is observed when sodium chloride is electrolysed.

If the decomposition proceeded in the theoretical manner the simultaneous presence of chlorine and caustic soda would give the reaction :—

$$Cl_2 + 2NaOH = \underset{\text{(Sodium hypochlorite)}}{NaOCl} + NaCl + H_2O.$$

As a matter of fact, however, subsidiary reactions occur to prevent the theoretical yield being obtained. According to P. Schoop, these disturbing factors include: (1) the oxidation of the bleaching agent to a higher stage, namely, to chlorite ($NaClO_2$) and chlorate ($NaClO_3$); (2) the reduction of the bleaching agent, already formed, to the stage of chloride; (3) the electrolytic decomposition of the products (hydrochloric acid and chlorine-oxygen compounds) occurring at the anode. It is true that the production of chlorate cannot be suppressed entirely, but it has been found that low temperature, appropriate dilution and neutrality of the salt solution are factors that tend to oppose the formation of chlorate.

As already mentioned, the cathode metal (metal of the negative pole) during the electrolysis of sodium chloride decomposes the water, with formation of caustic soda, whilst chlorine is liberated at the anode (metal of the positive pole). Recent experience has shown that when no diaphragm (porous partition) is used, the liberation of hydrogen causes a circulation of the liquid, so that after the initial escape of chlorine into the air, all the chlorine gas subsequently formed is immediately combined by the caustic soda to form sodium hypochlorite. So long as the temperature is low, and the solution remains faintly alkaline, the resulting chlorine should accumulate as hypochlorite. This, however, is not the case, chlorate being formed at first, and the hypochlorite itself then decomposing again, *i.e.*, the production of hypochlorite diminishes in proportion as it accumulates in the solution. To prevent this a diaphragm should be placed in the cell, or else the chlorine should be allowed to act on the lye in another vessel. In the former case the tendency to acidity noticed in the latter case is not observed; and this is important, one of the chief advantages of electrolytic bleaching liquor consisting in its being as neutral as possible. The extent of the reduction at the cathode is influenced by the amperage and by the temperature of the electrolyte. With a high amperage the liberation of hydrogen is so energetic that part of it escapes in the gaseous form, whereas with a low temperature the reduction is small. Hence, high amperage and low temperature must be maintained throughout.

Observations of Förster and Muller.—In addition to the phenomena already mentioned, Förster observed that when commercial chlorides are used, sparingly soluble hydrates (calcium and magnesium hydroxide) are formed at the negative pole, the resulting precipitate resisting the passage of the current and impairing the contact between the liberated hydrogen and the hypochlorite solution. Investigation of the course of the reaction has shown that if all the alkali formed were to come into immediate contact with the free chlorine there would be no formation of chlorate, this being prevented by the faintly alkaline reaction of the solution. As a matter of fact, the solution at the anode is even faintly acid, owing to the liberation of chlorine, the acidity being greater in proportion as the amount of hypochlorite in the acid zone increases. With regard to the voltage, another disturbing factor should be taken into consideration.

E. Müller has demonstrated by experiment that the anion of the hypochlorite, which is more readily set free than the anion of the chloride, is decomposed into free oxygen and hydrochloric acid. The use of current of high amperage necessitates the employment of a very strong solution of chloride, on account of the requisite resistance. If the formation of only a weak solution of hypochlorite be in view an excessive percentage of salt would make the process expensive. For this reason the right proportions must be determined in each case, when deciding on the construction of the apparatus. For the ordinary bleaching process there is no disadvantage in using weak liquor, whilst on the other hand this liquor possesses the important advantage of being free from lime; and being almost neutral, is more stable.

Types of Electrolyser.—Among the types of electrolyser now in use mention may be made of the following:—

The apparatus of Dr. Kellner (who is associated, in this connection, with Siemens & Halske, Berlin); the Haas and Oettel apparatus (Haas & Stahl, Aue, Saxony); the Schuckert apparatus (Schuckert & Co., Nuremberg); and the Schoop apparatus (now made by Siemens & Halske).

The Kellner Apparatus (E. Gebauer, Charlottenburg).—In this apparatus the electrodes, which are wound with platinum-iridium wire, are placed in a stoneware vessel, in the bottom of which is a pipe for the admission of the brine (sodium chloride solution) to be decomposed. After the solution has passed between the electrodes and become partially electrolysed it runs off through an overflow into a collecting vessel underneath. This is fitted with a hard lead cooling coil, traversed by cold water, to reduce to the normal temperature the liquor that has become heated in the electrolyser; which done, the liquor is returned to the electrolyser by a centrifugal pump. This cycle of operations is repeated until the liquor has been sufficiently enriched with active chlorine.

The Haas and Oettel Electrolytic Bleach.—In this system the electrolyser (Fig. 4) consists of a deep vat of best stoneware, in which the solution of salt is subjected to the electric current between specially prepared electrodes. The object of the process is to produce a clear and powerful bleaching liquor, mainly consisting of sodium hypochlorite. By means of vertical electrodes the vessel is divided into a number of separate cells, which do not communicate, but are provided with a feed orifice at the bottom of each, and a small overflow pipe at the top. The whole assemblage of cells is placed in a strong stoneware tank (Fig. 5) in such a manner that a free space is left between the bottom of the electrolyser and that of the tank. On the latter being charged with the solution of salt the liquid rises through the feed orifices in the separate cells until it reaches the centre of the overflow pipes (glass or porcelain) near the top. On the current being passed, the liberation of hydrogen causes the liquid in the cells to froth up violently and rise to such an extent that it escapes through the overflow in a continuous stream, at the same time drawing in a fresh quantity of fresh lye through the feed orifices. In this way

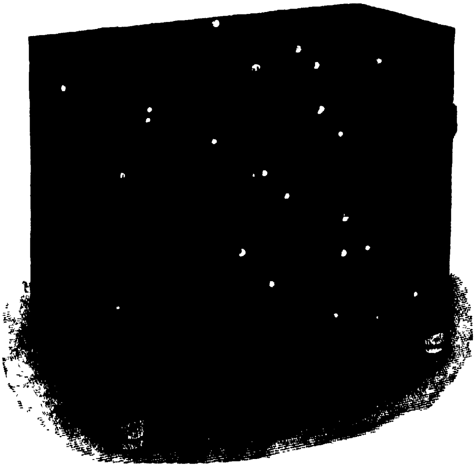

FIG. 4.—Haas and Oettel Electrolyser.

the inventors ensure a vigorous, automatic circulation of the liquor, and the rapid and uniform enrichment of same with active (bleaching) chlorine, combined with the advantageous utilisation of the electrical energy and of the salt employed. The circulation and uniform intermixing of the liquid are facilitated by fitting the overflows with branches and conduits which convey the overflow liquor to a considerable distance away from the corresponding bottom inlet. As a matter of fact, the differences in the content of active chlorine in various parts of the vessel are very small throughout the process. The collecting vessel is fitted, on the side where the liquor overflows from the electrolyser, with a cooling coil, between the turns of which the liquor is obliged to flow, for the purpose of cooling, before being returned to the bottom of the electrolyser. The temperature of the liquor between the cells should not be higher than 95° F. The bi-polar electrodes are made of a graphitic material, which is much cheaper than platinum whilst far stronger than the latter.

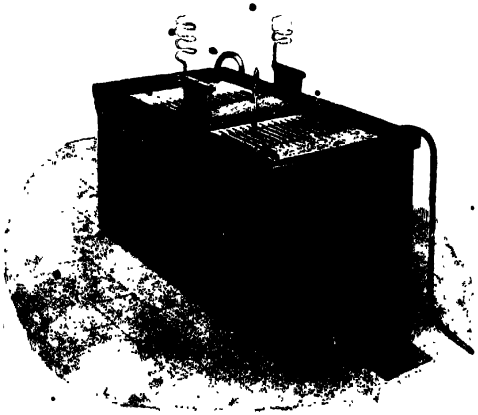

FIG. 5.—Haas and Oettel Electrolyser.

Working ten hours per diem the electrodes do not need to be replaced for eighteen months. The connecting terminals are of unoxidisable metal, the draw-off taps and bottom valves of stoneware; and consequently all parts of the apparatus are protected from the action of chlorine.

The salt is dissolved in a well-tarred wooden vat, fitted with stirrers that are operated by hand or belting. To prepare a solution of 10-11° Bé. strength about 60 lb. of common salt are dissolved in 50 galls. of water, the resulting liquid being

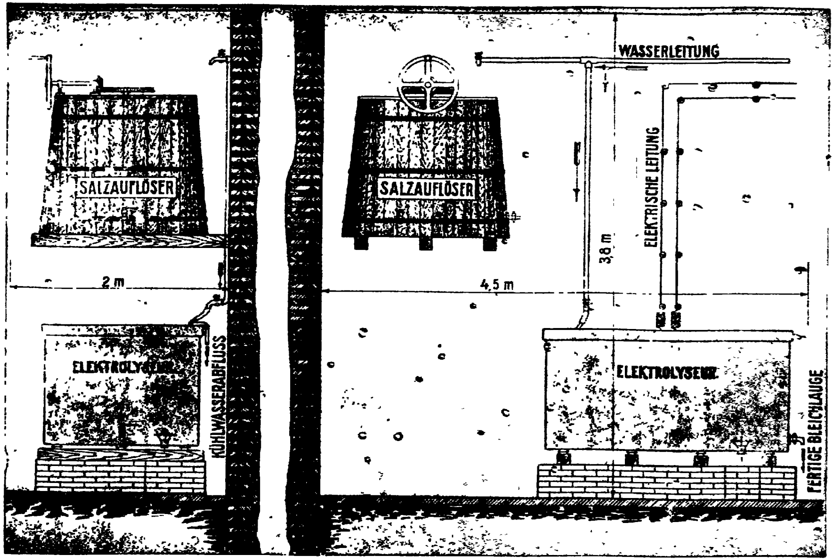

FIG. 6.—General Arrangement of an Electrolytic Bleaching Plant (Haas and Oettel). (Salzauflöser = Dissolving Tank. Wasserleitung = Water Pipe. Elektrolyseur = Electrolyser. Elektrische Leitung = Electric Conductor. Kühlwasserabfluss = Cooling Water Effluent. Fertige Bleichlauge = Finished Bleaching Liquor.)

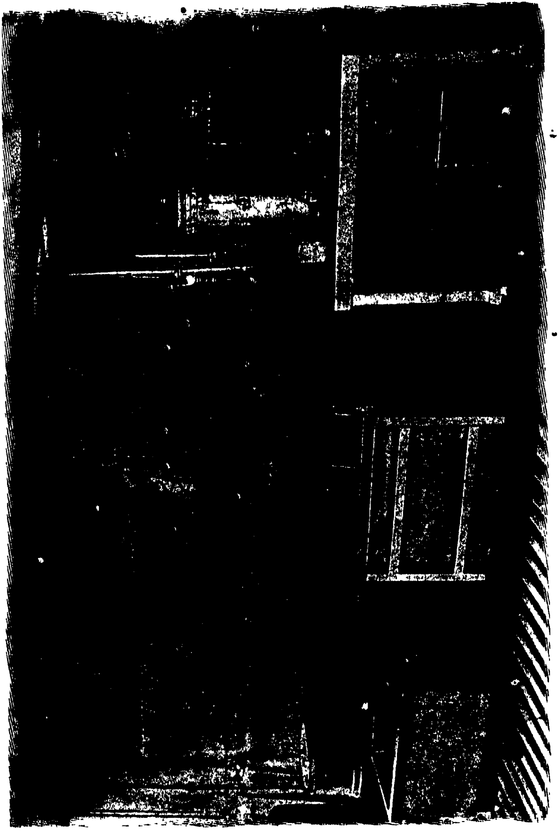

FIG. 7.—Small Electrolytic Bleaching Plant for Bleaching Yarn, etc. (Haas and Oettel).

left to clarify before running it into the electrolyser. When, after five or ten hours, a bleaching solution containing the desired amount of active chlorine has been obtained, the current is shut off, and the finished, perfectly clear bleaching liquor is drawn off into the collecting tank, leaving the apparatus ready for a fresh charge of dissolved salt.

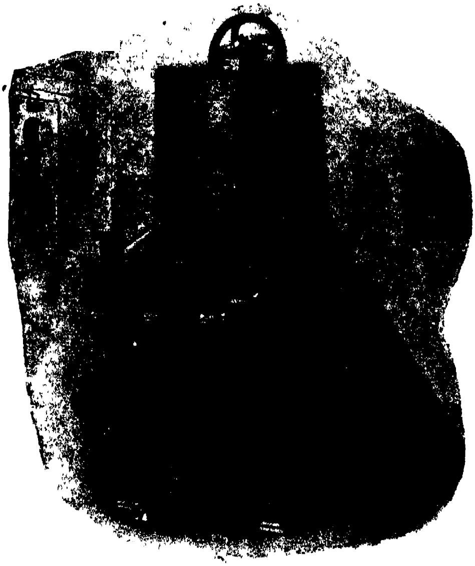

FIG. 8.—Small Electric Bleaching Apparatus for Laundries.

A sketch of the arrangement of an electric bleaching plant on the Haas and Oettel system is shown in Fig. 6; and a smaller set (capacity about 44 lb. daily) for bleaching yarns, etc., and consisting of an electrolyser, vacuum apparatus and centrifuge, is illustrated in Fig. 7.

A cheap set of apparatus (pattern TU) for small bleaching works and laundries is represented in Fig. 8.

This pattern, working with a 110-volt current (8-10 amperes) and about ½ cwt. of salt, will produce sufficient liquor to bleach about 5 tons of material daily, no expensive pumping apparatus or coolers being required. Its efficiency has been favourably reported on by A. Wagner, of the American Steam Laundry, who states that the bleaching liquor prepared in this apparatus, and of about 0·1 per cent. strength, does not rot linen and cotton fabrics; and since this liquor is diluted 12-15 fold for washing purposes, all risk is precluded. Moreover, the clothes are a better colour than when bleaching powder is used.

Schuckert Plant.—The arrangement of a bleaching-liquor plant, as manufactured by the Elektrizitäts-Aktiengesellschaft, formerly Schuckert & Co., Nuremberg, is illustrated in Fig. 9. Above the electrolyser is mounted the salt dissolving tank (an overflow tank being provided in large plant), consisting of a single wooden tank which is charged with the requisite amount of salt overnight, solution in the added water being effected by stirring with a paddle, so that the liquid has had time to clarify properly before work is commenced in the morning. A clear solution can also be prepared direct, by spreading the salt on a filter cloth laid on the top of the tank.

At a suitable height from the bottom the dissolving tank is provided with a draw-off tap, through which the solution is delivered, *viâ* a short length of pipe or hose into the electrolyser. In larger installations the tank may be made of concrete and fitted with mechanical stirrers.

The electrolyser (Fig. 10), which consists of two vats, is mounted on a suitable wooden platform. The salt solution (usually 10 per cent. strength) traverses the vats in a zig-zag course, and issues from the same, as a perfectly clear bleaching liquor containing 20 parts of active chlorine per 1,000 (corresponding to a 5° Bé. solution of bleaching powder), into a cement collecting tank underneath, whence it can be

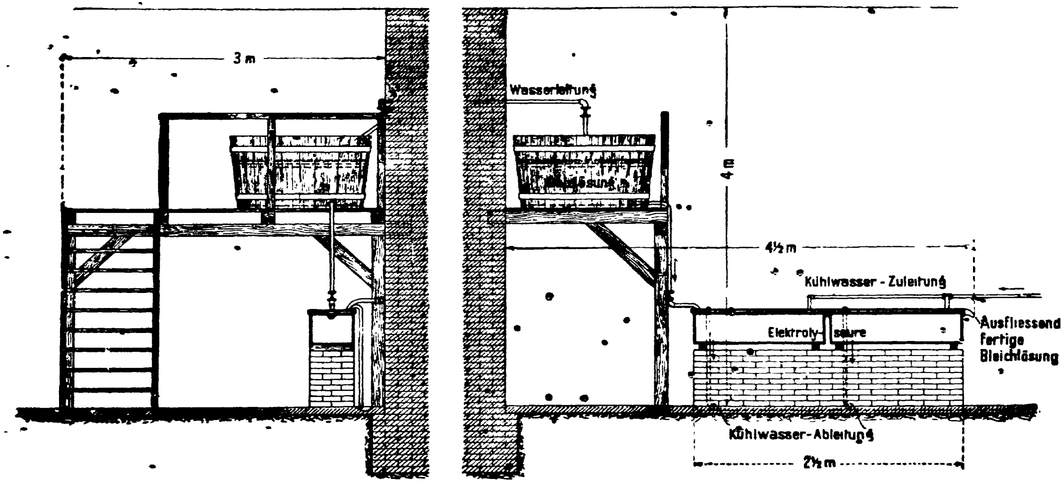

FIG. 9.—Arrangement of Schuckert Plant for Electric Bleaching Liquor. (Wasserleitung = Water Pipe. Salzlosung = Salt Solution. Kühlwasser-Zuleitung = Cooling Water Inlet Pipe. Elektrolyseur = Electrolyser. Kühlwasser-Ableitung = Cooling Water Outlet Pipe. Ausfliessende fertige Bleichlösung = Effluent Bleaching Liquor.)

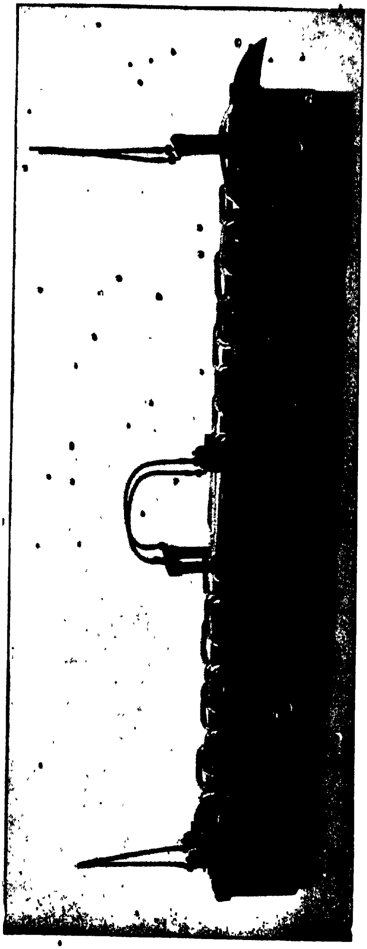

Fig. 10.—Schuckert Electrolyser.

conveyed (through pipes, or in any other way) to the bleaching tank, where it is diluted as required.

In order to obtain the highest yield from the current the travelling solution must be kept cool, for which purpose a cooling apparatus, connected with the water main, is attached to the apparatus.

The bleaching apparatus can be thrown out of action when desired, and on restarting work will yield bleaching liquor of the desired strength at once. The consumption of electrical energy is equal to 7 kilowatt hours per 1 kilo (2·2 lb.) of electrolytic chlorine, produced, from a 10 per cent. solution of salt, in the form of bleaching liquor containing 20 grms. of chlorine per litre (*i.e.*, a consumption of 5-5·3 lb. of salt per 1 lb. of chlorine); or 6 kilowatt hours in producing a similar liquor from a 15 per cent. solution of salt, the consumption of salt in this case being 7·5-8 lb. per 1 lb. of chlorine.

With salt at a low price a consumption of 5 kilowatt hours will furnish, from a 10 per cent. solution, a bleaching liquor containing 10-12 grms. per litre (10-10·6 lb. of salt per 1 lb. of chlorine); or 4·5 kilowatt hours will give a similar liquor from a 15 per cent. solution (15-16 lb. of salt per 1 lb. of chlorine). Neither the consumption of salt nor that of electrical energy, taken singly, will afford accurate data for judging the apparatus. For this purpose it is necessary to add the cost of both salt and power, these forming the most important items in the working expenses. A comparison of the calculations in respect of the cost of energy and salt per unit weight of chlorine shows that the Schuckert apparatus is economical in working. The data in connection with the above four eventualities, corresponding to different local conditions with regard to the cost of salt and power, are summarised in the following table, showing the consumption per kilo (2·2 lb.) of active chlorine :—

KW hours.	*Consumption of Energy.* Electrical KW hours.	Mechanical KW hours.	*Consumption of Salt.* lb.
7	9·5	10·5	11-11·66
6	8·15	9	16·5-17·6
5	6·8	7·5	22-23·32
4·5	6·1	6·[illegible]	33-35·2

Experience has shown that ¾ lb. of electrolytic chlorine is quite sufficient to replace 1 lb. of bleaching-powder chlorine (from 33·3 lb. of bleaching powder) in bleaching cotton. The relative cost of electrolytic and ordinary chemick bleaching can be gathered from the following practical instance:—

A bleaching works had a daily consumption of 118¾ lb. of bleaching powder, with an average content of 33½ per cent. (owing to loss during storage, the original strength being usually 35 per cent.). This quantity of powder, equivalent to 39½ lb. of chlorine, cost locally 7s. 8d., but the actual yield of active chlorine was reduced, by unavoidable losses, to 35¼-37½ lb. This weight can be replaced by about 28½ lb. of electrolytic chlorine, the production of which entails a consumption of 91 kilowatt hours (*i.e.*, 83 amperes with 110-volt current and working ten hours per day). At the same time 5·4 lb. of salt are consumed per 1 lb. of chlorine produced, *i.e.*, 154 lb.

	s.	d.
91 kilowatt hours = 136 mechanical h.p. hours cost, @ ⅜d. .	4	3
154 lb. of salt cost, @ ⅛d. . . .	1	7
	5	10

Hence, there is a margin of 1s. 10d. (or nearly 20 per cent.) for interest and depreciation of plant. As an example of the relative cost of electrolytic and bleaching-powder bleaching in the paper (cellulose) industry, the following comparison will serve:—

A paper works consumes 1 ton of bleaching-powder per twenty-four hours' day, equivalent to 6 cwt. of active or electrolytic chlorine. To produce this weight of electrolytic chlorine from a 10 per cent. solution of salt requires 2,100 kilowatt hours; or, working twenty-four hours per diem, with 87·5 kilowatts (131·5 mechanical h.p.) the consumption of salt being 32 cwt.

	s.
2,100 kilowatt hours cost (suction-gas plant) . . .	63
32 cwt. of salt at 9d. per cwt.	24
Labour (attendance—necessary with large plant). . .	3
	90

The bleaching powder costs 7s. 9d. per cwt., or 135s., so that there remains over for interest and depreciation 45s. or about 40-45 per cent. of the prime cost (working year of 300 days).

These examples show that, apart from the other advantages, bleaching with electrolytic lye is the cheaper for the textile industry, even when the cost of power is high and the price of salt anything but low. It is also cheaper in the cellulose and paper industries, provided cheap power be available, such as is now afforded by the use of suction-gas plant, which furnishes power at a cost of about ¼d. per h.p. hour, the economy being still greater with water power. It is also worthy of mention that a strength of 2 per cent. of chlorine can be obtained by merely passing the salt solution once through the apparatus, no re-pumping of the liquor being required.

The materials used in constructing the various portions of the apparatus are selected with a view to preventing wear in practical use. The electrodes are arranged and selected so that they shall not be liable to corrosion.

In some apparatus the electrodes have to be renewed every year, on account of wear; but the Schuckert possesses the advantage of the platinum apparatus, namely, material value, whilst free from the drawback common to many of these apparatus, namely, the wearing out of the platinum, this metal being used in the Schuckert apparatus only in such places where it is not exposed to wear and tear.

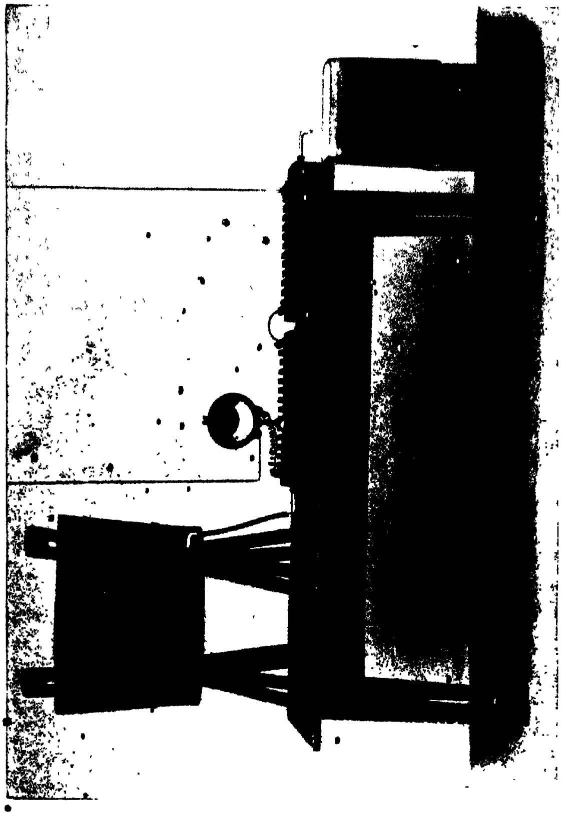

Fig. 11.—Small Schuckert Electrolytic Apparatus (Type G), with Graphite Electrodes.

The same makers also market a pattern with graphite electrodes (Fig. 11) specially adapted for laundries, and consisting of a wooden vat, taps for the salt solution, pipe connection to the electrolyser, and collecting vessel (of cement or earthenware) for the finished bleaching liquor, which must be diluted before use. The load and working of the electrolyser are controlled by a current meter; and a switch with safety fuses is provided. With a current of 5-15 amperes at 100 volts, and a consumption of 0·8-2·4 h.p., the apparatus produces a bleaching liquor sufficient for bleaching 8-24 cwt of washing.

The Schuckert apparatus has found extensive application in practice, being used in the cellulose industry (soda- and sulphite cellulose) and in the textile industry. In the latter branch it is employed for bleaching loose cotton, card sliver, bobbins, hank yarn, twist, fabrics, lace, etc.

Schoop's Electrolytic Bleaching Apparatus.—In this system, which is used in bleaching works at Augsburg, the salt is dissolved by placing it in a bag, which is suspended in a vessel of water, the operation taking eleven hours to complete. The resulting solution is forced by a small centrifugal pump through a cooling pipe into the electrolyser, after issuing from which it runs into a tank underneath.

The salt solution runs from the collecting tank into a porcelain tank, or distributor, whence it is discharged, in thin streams, through pipes, into the upper electrolytic tank, and then overflows into the four decomposing batteries underneath and electrolyser tank, whence it is pumped back continually into the electrolyser. When the electrolyser tank is full the connection between the pump and the salt solution tank is cut off by closing a tap, another tap being turned on to connect the pump with the electrolyser tank, so that the pump now forces liquor from the latter to the electrolyser, by way of a cooling coil. The solution passes through the electrolyser without interruption, whilst the electric current, generated by a dynamo and passed through the electrolyser, converts the solution of salt in about eleven hours into finished bleaching liquor, which is drawn off into a storage tank underneath the electrolyser tank. Schoop claims three novel properties for his system. In the first place, the salt solution to be electrolysed is broken up into thin streams of liquid, so that a rapid flow of the solution is rendered possible, which, in conjunction with the gas bubbles ascending along the troughs, effectually and automatically prevents the separation of the electrolytes. In connection therewith the distance between the electrodes is diminished to a small fraction of that necessary in plate systems. Finally, the principle of electrodes of unequal size is introduced for bleaching apparatus, the cathode side being smaller than the anode side, so that the re-conversion of bleaching material that has once been formed is precluded, and the production of more concentrated solutions of chlorine is rendered possible. This system, however, on account of certain inadequacies, has not made any great headway in practice.

Kellner Bleaching Apparatus.—This electrolytic apparatus, the invention of the well-known electro-chemist Dr. Karl Kellner, is put on the market by Siemens & Halske, Berlin.

A. Construction.—The electrodes are composed of platinum-iridium wire gauze, laid horizontally in special troughs, or electrolysers, which are effectually lined with glass and earthenware. These form a series of decomposing cells, arranged side by side in steps, so that the salt solution and bleaching liquor must traverse the separate cells in a horizontal, sinuous line. This arrangement enables the work to be carried on in the most advantageous manner, utilising the salt and the electrical energy to the fullest extent. The electrodes themselves are connected up on the bipolar system, so that no connections between the several pieces of gauze are required inside the apparatus, these being always a defect. The only contacts necessary in this electrolyser are those through which the current is supplied; and these are specially formed and built in the apparatus in such a manner that they cannot possibly be destroyed through any action of the electrolytic process. The electrodes can be readily taken out and replaced at any time for inspection.

B. Method of Working.—The first step in the preparation of hypochlorite is to make a solution of salt (from 6 to 18 per cent. strength), which is then electrolysed by the aid of non-corroding electrodes, without the use of a diaphragm.

According to the usual idea, the common salt is decomposed into chlorine and sodium ($NaCl = Na + Cl$), the metal immediately combining with the water, with formation of caustic soda ($Na + H_2O = NaOH + H$). According to the ionic theory, however, it is more probable that, instead of free sodium being formed first, the hydrogen ions are discharged direct at the anode, the hydroxyl ions formed at the same time from the water, by ionisation, being left in the liquid. In this reaction hydrogen is liberated, and escapes in the form of bubbles of gas. The cathode being at the top, the hydrogen can escape freely.

The chlorine formed at the anode dissolves in the surrounding stratum of electrolyte and diffuses upward, thus encountering and reacting with the sodium hydroxide formed at the cathode, sodium hypochlorite being produced in accordance with the equation:—

$$Cl_2 + 2NaOH = NaCl + H_2O + NaOCl.$$

If the reactions went on solely in this manner it would always be possible to obtain any desired strength of hypochlorite liquor economically; but this is by no means the case, and up till very recently it was impracticable to obtain liquor with more than about 1 per cent. of active chlorine. The attainment of higher strengths, up to 5 per cent. of active chlorine, only became feasible after extensive investigation of the phenomena of electrolysis.

On the basis of researches by Professor Foerster and his pupils, combined with experiments of their own, Siemens & Halske have improved the Kellner patent electrolyser considerably.

An approximately motionless stratum of liquid surrounds the anode at the bottom of the vessel. The chlorine formed at the anode dissolves in this stratum and furnishes, with the diffused hypochlorite, hypochlorous acid, which is only very slightly dissociated :—

$$NaOCl + Cl_2 + H_2O = NaCl + 2HOCl.$$

Since only the few hypochlorite ions present are discharged, the resulting losses are small. In a similar manner, the hydroxyl, invariably present as the result of hydrolysis, is rendered innocuous by the chlorine, in accordance with the equation :—

$$NaOH + Cl_2 = NaCl + HOCl.$$

The chlorine, or hypochlorous acid, formed in this (partly) stagnant understratum of liquid gradually ascends by diffusion and partly by convection, and forms sodium hypochlorite with the hydroxyl produced at the cathode.

The access of hypochlorite ions to the anode might be prevented in other ways than by mechanical resistance.

Analogous to the oxidation of hypochlorite at the anode, the reduction at the cathode can be prevented or opposed, the best method being the addition of calcium compounds.

In order to prevent the retrogression of the actual bleaching agent, sodium hypochlorite, by the action of the nascent hydrogen at the cathode, according to the equation: $NaOCl + H_2 = NaCl + H_2O$, it is therefore necessary to add lime compounds, in large quantity, to the electrolyte (salt solution). The lime compounds added, or already present in the salt, are decomposed during the electrolysis, with formation of calcium, which is transformed into the hydroxide by the action of the water, this hydroxide being deposited as a coating on the cathode gauze :—

$CaCl_2 = Ca + Cl_2$ and then $Ca + 2H_2O = Ca(OH)_2 + H_2$. This coating prevents the ready-formed hypochlorite from gaining access to the cathode, and consequently from being reduced to sodium chloride once more.

The addition of calcium compounds is almost invariably practised, though perhaps unknowingly; since it may be affirmed that the favourable effect of these compounds, which find their way into the salt solution as impurities in either the salt or the water, is practically always in evidence during the preparation of hypochlorite.

To increase the mechanical cohesion and resistance to diffusion of the calcium hydroxide deposit on the cathode, small quantities of certain organic bodies are added as well, these also helping the hydrogen that is liberated at the cathode to escape quickly in the form of large bubbles, instead of remaining suspended, in a finely divided state, in the electrolyte. This again favours the effect in view, since the liberated hydrogen has no opportunity of reaching the anode and recombining with chlorine there.

Owing to the organic additions the calcium hydroxide deposit is precipitated in the form of a solid cathode coating, generally of sufficient mechanical cohesion to prevent it separating from the cathode during the electrolysis. These small additions have also the advantage of rendering the coating almost impervious to hypochlorite, and thus increase its action.

These organic substances are of different kinds, and a distinction must be drawn between: (*a*) those accidentally present in the electrolyte, and originating in the salt or water, or in the structural materials used, such as wood, cementing material, vulcanised rubber, etc.; and (*b*) those added purposely, such being usually more or less soluble, but not too readily oxidisable, complex organic bodies of the alzphatic series.

The horizontal position of the electrodes and the resulting stratification serve the additional purpose of allowing the hypochlorite solution to run away over the electrodes without reaching the anode in the bottom, where the sodium hypochlorite would be converted into the useless compound, sodium chlorate ($NaClO_3$).

Hence, owing to the arrangement of the electrodes and to suitable additions to the electrolyte, the attainable yield of chlorine is but little below the theoretical figure; and in this way it is possible to obtain liquor of a strength hitherto regarded as out of the question.

The direct conversion of the hypochlorite into chlorate is effected on purely chemical lines by catalysis. According to the researches of Foerster and Jorre the transformation proceeds in accordance with the equations:—

$$(\alpha)\ NaClO + 2HOCl = NaClO_3 + 2HCl$$
$$\text{and } (\beta)\ 2NaClO + 2HCl = 2NaCl + 2HOCl.$$

As can be seen at once from the former equation, the amount transformed into chlorate is proportionate to the time, the concentration of the hypochlorite and the square of the concentration of the hypochlorous acid, according to the law of mass action. Moreover, Foerster and Jorre found that the velocity of decomposition increases about 2½-fold for every 10° C. rise in temperature.

Hence it follows that the electrolyte must be kept as neutral as possible, or only slightly alkaline at most, any higher concentration of alkali being injurious. The temperature, also, should be as low as possible. Now in practice it is difficult to maintain any desired low temperature; and since it is known that cold solutions are far worse conductors than hot, and that the conductivity of salt solutions diminishes by rather more than 2 per cent. for each 1° C. fall in temperature, it is a disadvantage to work with solutions that are too cold. It may therefore be assumed that the most suitable temperature for the solution is between 20° and 25° C. (68-77° F.). It is therefore apparent with electrolysers in which glass cooling worms are used that, apart from the great fragility of such worms, economical electrolysis is very difficult, owing to the impossibility of efficient cooling. The addition of alkali, which counteracts the ill effects of high temperature, cannot be recommended, since alkaline liquors do not bleach well. It may also sometimes happen that decomposition of the hypochlorite occurs, with liberation of oxygen, in accordance with the equation: $2NaOCl = O_2 + 2NaCl$.

This reaction occurs on purely catalytic lines, under the influence of certain heavy-metal compounds, of which even small traces may be harmful. The best known in this connection is cobalt; but nickel, copper, manganese and others are also injurious.

On this account the bleaching liquor should, as far as possible, be kept from contact with the said metals or their alloys. The spontaneous decomposition of the bleaching liquor during storage is greater than during its preparation, since bleaching liquor that contains even minute quantities of free hypochlorous acid may suffer considerable loss of hypochlorite. A simple method of increasing the stability would be by adding alkali, were it not that alkaline liquors are known to be imperfect bleachers.

Experiment has shown that the spontaneous decomposition and bleaching power run on exactly parallel lines, that is to say that just as the bleaching liquor decomposes in proportion to the square of its content of hypochlorous acid, so is the rapidity of its bleaching action dependent on the same factor; and the increase in the rapidity of bleaching with the temperature is about equal to the increase in the rate of spontaneous decomposition.

For these reasons all unduly large additions of alkali should be avoided; and in fact, on the contrary, the bleaching liquor should not be too stable in order that it may bleach quickly and well enough.

It may also be mentioned that the saving in active chlorine, almost invariably effected by electrolytic bleaching liquors in comparison with bleaching powder, is only feasible when the liquor is not alkaline.

If the bleaching liquor is to be kept for any length of time care must be exercised in the addition of any alkali, a low storage temperature being preferable as a means of preventing such decomposition.

C. Mounting the Apparatus.—The arrangement and working of a modern set of bleaching plant on the Kellner system are simple. The quantity of salt necessary for a given production of bleaching liquor is dissolved in a tank, and the solution is transferred to a second tank to clarify. For this purpose any large wooden tub, or suitably lined brick tank, or even the apparatus generally used for dissolving bleaching powder, may be employed. The clarified solution is run into the cooling tank attached to the electrolyser, and is forced continuously through the electrolyser by a small centrifugal pump. The solution is decomposed by the electric current, and is transformed direct into a highly concentrated bleaching liquor ready for use. In the cooling tank the liquor is constantly recooled by means of leaden coils traversed with ordinary tap water, and is thus maintained at the requisite low temperature. The circulation is kept up until the desired strength in active chlorine is attained, whereupon the liquor can be forced, by the same pump, from the cooling tank into a storage tank, or direct to the bleaching vessel.

As mentioned above, a small centrifugal pump is required to maintain an efficient circulation of the liquor in the Kellner electrolyser; but the amount of motive power for this is so small as to be negligible in estimating the working expenses, whilst, at the same time, the brisk movement of the liquor ensures reliable working and higher efficiency.

The Siemens & Halske apparatus furnishes bleaching liquors suitable for all the requirements of the textile industry, as well as for paper-making and cellulose manufacture; and, in fact, there is no difficulty in producing a liquor containing a higher chlorine content than a bleaching powder solution of over 10° Bé. strength.

Fig. 12 shows a complete set of plant in a large cotton

Fig. 12.—Siemens & Halske Electrolytic Bleaching Plant. (Arranged for Bleaching Cotton.)

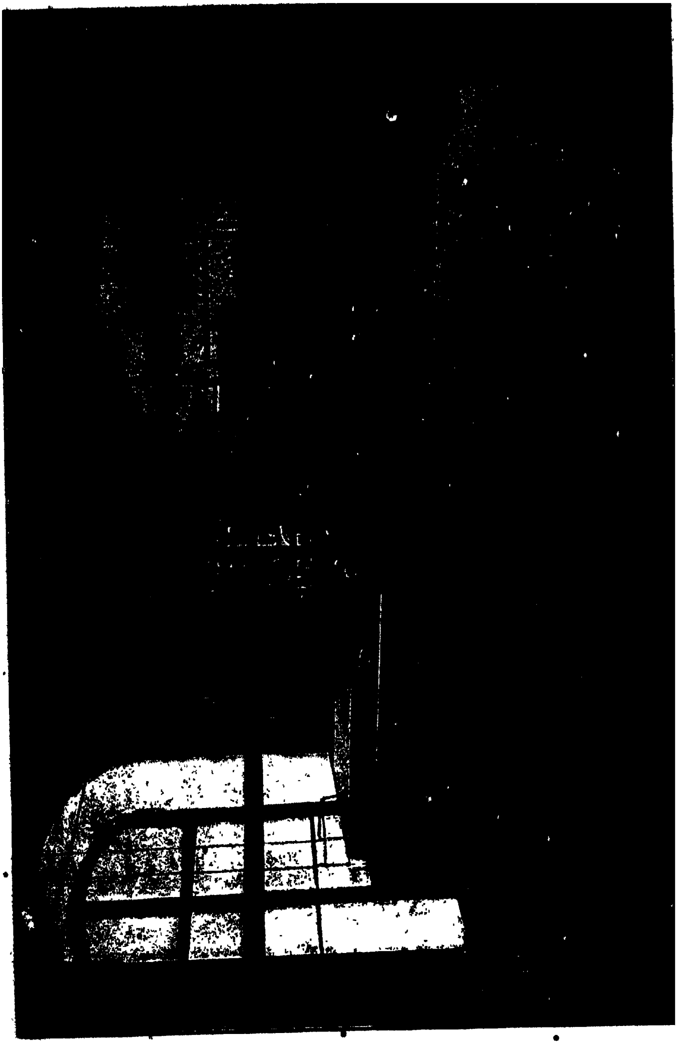

FIG. 13.—Siemens & Halske Electrolytic Bleaching Plant. (Arranged for Bleaching Linen.)

bleaching works, including concrete tank and pump, one-third of the electrolyser being covered in. A larger plant, for bleaching linen, is shown in Fig. 13; and a small electrolyser, of simple construction, chiefly for laundries and chemical cleaning works, in Fig. 14. This apparatus (the rear portion of which is covered in) has been found highly suitable for working on a small and experimental scale. A larger pattern, of similar type, for medium sized bleaching works, is illustrated in Fig. 15.

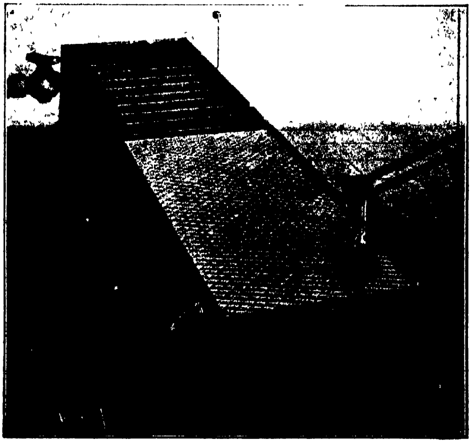

FIG. 14.—Siemens & Halske Electrolytic Bleaching Plant (Special Pattern for Laundries, Chemical Cleaning Works and Small Bleaching Works.)

Determining the Bleaching Power of Electrolytic Liquors.—The liquor may be titrated with arsenious acid, according to the Pernot method, or by the Mohr method (sodium sulphite or thiosulphate). When decinormal solutions are used each c.c. of decinormal arsenite or thiosulphate corresponds with 0·003545 of active chlorine.

Volumetric Method.—This method is now generally adopted

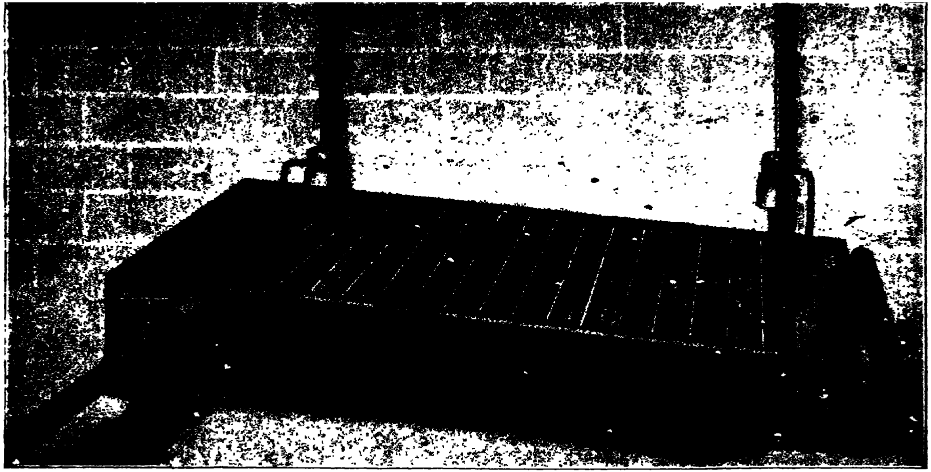

Fig. 15.—Siemens & Halske Electrolyser. (Special Pattern for Small and Medium Bleaching Plants for the Textile Industry.)

in bleaching works. It is based on the fact that hydrogen peroxide liberates from the electrolytic liquor exactly the same volume of oxygen gas as there is active chlorine present.

The volumeter, for carrying out this test, is shown on a small (1 5) scale in Fig. 16. The results are generally rather higher than the truth, but are sufficiently accurate for practical purposes. The test is performed as follows :—

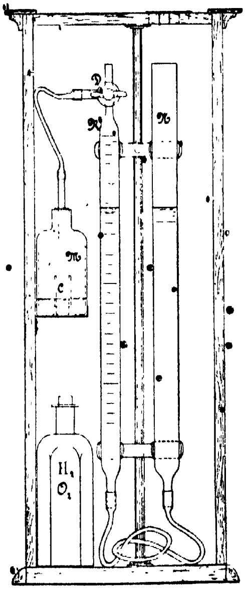

FIG. 16.—Volumeter for Measuring the Bleaching Power of Electrolytic Bleaching Liquors.

The mixing glass M, which contains a small concentric cylinder, is charged with 3·5 c.c. of the bleaching liquor, care being taken that none gets into the inner glass. The latter is filled three parts full, with hydrogen peroxide solution, introduced by means of a pipette, the glass stopper being then put into position and the mixing glass thereby placed in communication with the measuring tube R. The three-way tap D is turned so that the small glass knob is on the left, thus putting the mixing glass and the measuring tube in communication with the air. By slowly lifting the adjustment tube N the water level in R is adjusted to the point O, which done, the three-way tap is turned till the knob is underneath and the tube N is returned to its lowest position, the mixing glass being then tilted so as to mix the two liquids together.

Mixing is facilitated by energetic shaking. Effervescence occurs at once, and the water level in R descends, becoming stationary after a few seconds. The tube N is then raised until the water level in R and N is equal, and the volume of gas in R is afterwards read off. The resulting figure gives the content of active chlorine in parts per mil.

Bleaching with Electrolytic Bleaching Liquor.—As already stated, the actual operation of bleaching with electrolytic liquor is carried out in the same apparatus as is used for chemicking. In the case of paper stock the bleaching liquor is stored in cement tanks, from which the liquor is run into the paper-making machine, to be mixed with the material to be bleached. The pulp is then drawn off into vats, and left to itself for one to several hours, according to the quality of the material, before drawing off the liquor and washing the mass. The preliminary treatment of the material is the same as usual. According to E. Schoop, electrically bleached material is much less trouble in sizing than when bleached with bleaching powder.

Textile fibres do not require very strong bleaching liquor. For cotton in cops or bobbins the chlorine content need not exceed 0·4-0·8 per cent., whilst loose cotton can be bleached a full white with liquor as low as 0·2-0·4 per cent. A liquor containing ½ per cent. of chlorine will do for cotton yarns, such as knitting yarn, if the yarn be bleached in hanks on the usual English system.

As a rule the amount of active chlorine may be lower in electrolytic liquors than when chloride of lime is used. Schuckert states that experience has shown that 0·75 part of electrolytic chlorine can replace 1 part of chlorine from bleaching powder (contained in 3-3·3 parts of powder). Siemens & Halske say that the effective saving of active chlorine varies with the kind of material and the preparatory treatment of same.

Speaking generally it may be assumed that the saving in active chlorine and acid averages: in the case of light cottons 20-50 per cent. and 40-60 per cent. respectively; with heavy cotton yarns 15-25 per cent. and 30-40 per cent.; with loose cotton 10-30 per cent. and 30-40 per cent.; with linen yarns 15-25 per cent. and 25-50 per cent.; with straw 8-20 per cent. of chlorine; with linen rags 15-25 per cent.; and with cotton rags 15-35 per cent. of chlorine.

Latterly the practice of bleaching cotton in the loose state has grown in favour, the yarn being then spun from the bleached fibre.

A preliminary bowking with hot 1 per cent. caustic soda is required, as also a subsequent souring with ½ per cent. sulphuric acid. The chlorine is washed out of the bleached goods.

In the lime bleach sometimes practised, the preliminary boiling of the material is unnecessary, the only treatment required being an impregnation with moderately warm caustic soda, which is forced through the closely packed mass of cotton under a pressure of several atmospheres. In this process two to three times as much chlorine is requisite as in bleaching well-boiled goods. This lime process is not to be recommended, the cotton turning yellow and even becoming brittle.

Jute and ramie fibre must first be treated with warm soap solution, which dissolves the bast; and in the case of jute removes the petroleum added in the "batching" process. The washed fibres are then bleached with a weak liquor containing 0·1 per cent. of chlorine. It should be mentioned that in treating ramie for the production of fibre the rind is removed in a machine invented by Faure, the fibres being then freed from adhering vegetable mucilage by soaking in alkaline water instead of soap solution. More recently it has been proposed by Sansone to boil the stalks for a short time in potash lye, to facilitate the detaching of the bast from the woody matter. The same author also recommended the storing of the freshly cut stalks in bricked pits in a solution of sodium bisulphite, this treatment preventing fermentation. Ramie fibre requires special care in bleaching.

Jute is cleaned for bleaching by the aid of only weak alkaline liquors, such as a solution of alkali silicate, which does not corrode the fibre. The jute is in nowise injured by the above bleaching process. After removal from the bleaching liquor it is washed with water, and preferably entered in a bath of dilute sodium bisulphite, where it may remain for several hours before washing. This bisulphite bath is, however, not indispensable.

Hemp yarn requires to be either well boiled in a 1 per cent. solution of carbonate of soda, or else suitably cleaned with a solution of alkali silicate, before bleaching. A 0·2 per cent. bleaching liquor is used. Owing to the difficulty of bleaching this fibre the process has to be repeated several times; but provided sufficient liquor be used and the exposure is long enough, it is possible to obtain a full white bleach with the above liquor.

DIRECTOR OF INDUSTRIES
Bengal

PART II.

DETERGENTS.

OF STRIES Bengal

INTRODUCTION.

Owing to the difficulty of making an immediate selection of the most suitable detergent from among the large number—both new and old—available, it is desirable to preface the description and application of these agents by a brief consideration of the points that should be borne in mind in making that selection, so that stains of various kinds may be removed effectually without injury to the material.

In the first place one must possess a sufficient knowledge of the composition of the detergents themselves. For example, a rust stain on linen or other fabric cannot be removed with ammonia, or a copal varnish stain on cloth with dilute alcohol. Rust consists of iron hydroxide, which is insoluble in ammonia; and copal varnish is insoluble in dilute alcohol. In the former case the detergent employed to remove the rust must be one that combines with the iron to form a soluble compound, which can then be washed out with water. To cleanse a fabric stained with copal varnish a solvent for copal is requisite; and since copal will not dissolve even in cold, rectified spirit containing 95-96 per cent. of alcohol, this liquid will not remove the stain. It should be remembered that copal oil varnish is prepared by boiling melted copal with boiled linseed oil, or by treating the resin with a mixture of oil of turpentine and linseed oil; whereas volatile copal varnish (spirit varnish) is made by dissolving melted copal in a mixture of alcohol and ether or chloroform, benzol, etc., so that one or more of these solvents will be needed to remove the stain.

When the stain is on an undyed fabric it is sufficient in many cases to treat it with a suitable solvent; but if the fabric be dyed it is then necessary to consider whether the dyestuff used is soluble in the detergent one proposes to employ. Should it be soluble therein, great care will have to be used in applying the detergent.

The material or fabric on which the stain is situated must also be taken into consideration

Behaviour of Various Fabrics in the Presence of Chemical Reagents.—In this connection attention will first be devoted to the older detergents, such as ammonia, caustic potash or soda, solutions of alkali carbonates, ammonium carbonate, dilute acids, etc., some of which can only be used under certain conditions—because the action of these on fabrics is least widely known, and has only recently been properly determined.

For woollen materials—*i.e.*, woollen cloth, twill, upholstery damask (also containing silk and cotton), velvets (plush), carpets and tapestry (velvet Brussels, French Gobelins, etc.)—such detergents as caustic potash or soda, strong ammonia or hot solutions of alkali carbonates should never be used for removing stains.

The fibre of wool is attacked by even dilute caustic alkalis and also by dissolved alkali carbonates when the latter are used at a temperature exceeding 122° F. Cold, moderately strong ammonia, and cold, dilute alkali carbonates will not attack the fibre direct, though concentrated ammonia will after an exposure of about three minutes; and even dilute ammonia will affect it after a short time. Ammonium carbonate alone has practically no action on sheep's wool.

On the other hand, wool resists the action of dilute acids, and may be boiled in acidified water for some time without undergoing any change.

If it be necessary to use caustic alkalis for removing stains from cloth the operation must be performed with the greatest care and at a low temperature. The less powerful solutions of alkali carbonates must not be concentrated or too warm, since otherwise the strength of the wool fibre will be impaired, the fibre also becoming rough and hard, and losing its gloss.

In the case of silk goods (repp, twill, damask, brocade, velvet, etc.) the action of dilute caustic alkalis takes away the gloss; and even moderately concentrated lyes will dissolve silk in the warm. It should also be remembered that silk is corroded by prolonged boiling in soap solution. Warm, dilute acids have an injurious effect on this material.

Black silk must not be brought into contact with acid, and coloured silks will hardly stand water. Good black silk is usually dyed with logwood, whilst coloured silks are known to part with their dye in water. Any rubbing or scraping will cause loss of colour, so that silk goods must be cleansed only with a sponge or a moderately soft brush.

Cotton goods—calico, batiste, percale, jaconnet, repp, dimity, twill, Manchester- or cotton velvet (velveteen), etc. Here it must be borne in mind that cotton fibre is not greatly affected by dilute acids (*e g.*, hydrochloric acid) in the cold, whilst acetic acid has no action on this fibre. Cotton is also able to stand dilute caustic alkalis in the cold; but concentrated lyes (20-30° Bé.) produce a chemical change in the fibre and cause it to shrink.

The term linen is generally applied to closely woven, smooth fabrics, made either of pure flax or with a flax warp and tow weft; as also to flax and cotton union fabrics, with flax warp and cotton weft. Since the cleansed flax fibres consist for the most part of cellulose, though, by reason of the lignin they contain, they cannot be classed with the non-ligneous fibres (such as cotton), linen goods will generally stand the same treatment as cottons. Fine yarns are made from the best quality jute and are used for making curtains, carpets and upholstery fabrics, for which their lustre renders them very suitable. Jute fibre consists of cellulose, with bastin, the so-called corchorobastose, which is readily decomposed by acids, and is very susceptible to chemical reagents of all kinds. This must be borne in mind in the chemical cleaning of these goods.

Methods of Removing Stains.—The above particulars indicate the general methods to be adopted for the removal of stains in general. To recapitulate, it is necessary first of all to have a knowledge of the properties of the detergents (liquid, solid or pulp form), especially as regards their solvent capacity and chemical action; secondly, the influence that the detergent may exert on dyed materials under certain conditions should be borne in mind; thirdly, the question must be considered whether the detergent selected has any injurious action on the material to be cleaned.

Chemical Cleaning and Detergents.—Stains, whether of a mechanical or chemical nature, can be removed from a great variety of fancy articles and clothing by chemical cleaning. The object of this treatment is to dissolve out grease, and remove perspiration and dust, by treating the stained articles with hydrocarbons. It not infrequently happens, however, that even after this treatment the fabric still exhibits stains, some of which may be of vegetable origin—for instance, fruit and vegetable juices—or caused by animal matters, such as blood, fat, secretions, etc.; whilst stains may also be caused by chemical decomposition, all of which stains it is desirable to remove by the aid of detergents.

Until quite recently the only detergents used—apart from water—were alcohol, ether, benzine, benzol, chloroform, acetic acid, ammonia, oil of turpentine, soap, dilute and alkaline lyes and dilute organic acids. Oxalic acid, borax, soapwort and ox-gall were also used for certain purposes. A large number of liquids and substances was therefore available, all of them suitable for the objects in view if properly applied. At present more is expected of the cleaner, and perfect results are demanded in the shortest possible time.

In order to meet these increased requirements it became necessary to discover new detergents and processes, so as to be able to remove all kinds of stains from every imaginable article of clothing, including expensive costumes and the like, in a simple and rapid manner, and more completely than was possible heretofore. In addition to the detergents already mentioned, acetic ether, potassium cyanide, carbolic acid and glycerine were already in use to some extent, but all the rest, including benzine soap, carbon tetrachloride, amyl acetate, hydrogen peroxide, tetrapol, hexol, etc., are of recent introduction.

CHAPTER I.

BENZINE SOAPS.

It is well known that benzine will dissolve all kinds of fats, but not mucilaginous and fat-like substances; so that this detergent will not completely eradicate stains caused by paint (containing oxidation products of linseed oil), tar, perspiration or the like. Even when such stains have been apparently removed by this treatment, they soon reappear when the material is exposed to dust in wear.

In these circumstances it became desirable to supplement—as in ordinary washing—the fat-dissolving properties of benzine with the actual cleansing power of soap, great success being expected from this combination in the chemical cleaning branch. For this purpose it became necessary to incorporate soap with the benzine; but since ordinary soap is insoluble in benzine, and the employment of water is impracticable, attempts were made to dissolve thoroughly dried soap in alcohol, oil of turpentine, benzol or the like, benzine being added to the mixture. The products obtained in this way, however, were only mixtures and not solutions of the soap; and in the most favourable circumstances nothing more than an emulsion resulted. After long-continued investigation and experiment, Gronewald & Stommel, Marienhöhe Works, Elberfeld, succeeded in producing a good soap (Marienhöhe saponin) completely soluble in benzine. This product is a solid mass, a little softer than wax, and nearly white, or yellowish white, in colour. It is an acid salt (alkali oleate), containing in addition a little, chemically combined, water of hydration. The reaction is faintly alkaline, and the soap is insoluble in distilled water.

This saponin is only partly distributable in water, forming a milky liquid, which lathers strongly when shaken. On the other hand, this benzine soap is soluble in 98 per cent. alcohol, amyl alcohol, ether, benzine, chloroform, acetic ether and carbon tetrachloride. Owing to this solubility of the saponin in question, benzine, which previously was used solely as an extractive agent, has acquired actual washing properties, similar to those possessed by water when used along with soap.

The solvent power of benzine is considerably enhanced by an addition of Marienhohe saponin. At the same time the presence of the soap increases its capacity for absorbing water, without impairing its power of extracting fats and fatty substances.

Removing Stains with Benzine Soap and its Solutions.—Alcohol is known as a solvent of resinous and greasy stains; and is preferably employed, for this purpose, in as pure a condition as possible (97-98 per cent. strength). To increase its detergent power benzine soap is dissolved in 98 per cent. alcohol, either alone or mixed with ether, chloroform, etc. As a rule, better results are obtained when two or more of these solvents are used together, especially when their solvent character is of the same order.

As mentioned above, benzine soap is completely soluble in benzine. Petroleum spirit is also largely used, in conjunction with benzine soap, for removing resinous and greasy stains, the effect being increased by employing a mixture of benzine and benzol, both of which solvents act in the same manner.

Rectified oil of turpentine, alcohol, etc., are also added, with the same object; but these mixtures must not be used unless they are perfectly clear. Benzine soap dissolves completely in such clarified mixtures, and can then be employed to remove all kinds of stains resulting from grease, resins or asphaltum, etc.

Stains produced by blood, coffee, chocolate, gravy, glue or cart grease can be eradicated by washing with warmed benzine soap, followed by rinsing with benzine.

In addition to the mixtures referred to above, carbon tetrachloride and chloroform are used for removing tar and paint stains. Thus, for instance, tar can be removed completely from white articles with a mixture of chloroform and carbon tetrachloride, and also with benzine if the articles have previously been brushed over with the tetrachloride. Recent experience has shown, moreover, that the extractive power of cold benzine for a number of substances is increased by applying the benzine in a finely divided state.

Antibenzine Pyrine, or Richterol.—Marienhöhe saponin possesses the valuable property of eliminating the electrical excitation of benzine when added in small quantities to this solvent. For the same purpose, Richter, in 1893, recommended the use of magnesium oleate, which preparation has been put on the market under the name Richterol, or Antibenzine pyrine.

To make this preparation 22 lb. of white curd soap (containing 70 per cent. of fat) are dissolved in water, magnesium chloride or sulphate being added to the solution so long as a precipitate of magnesium oleate (magnesia soap) continues to form. This latter is purified with boiling water, dried, melted at 130° C., treated with 15 lb. of cold petroleum, and dissolved in 20 galls. of benzine. One lb. of the product is sufficient to protect 7,000 galls. of benzine from spontaneous ignition by electrical excitation.

The patent rights secured by Grönewald & Stommel for their benzine soaps extend to all solvents of fats, especially to benzine-soluble soaps prepared as hydrated oleates of acid salts of the alkali metals, *i.e.*, to all such soaps as are made from potash, soda, ammonia, or mixtures of same, and vegetable and animal fats, in so far as these soaps are soluble in benzine.

Other firms afterwards took up the manufacture of liquid benzine soaps, among which may be mentioned the "universal" benzine soap of Simon & Durkheim (Offenbach), the Weralin of O. Gans, and the liquid benzine soap of E. Koehler. In contrast to the solid benzine soaps, the "universal" benzine soap of Simon & Dürkheim is a neutral soap, and not an acid soap containing a large proportion of unsaponified oleic acid. All its fatty constituents are completely saponified and operate in chemical cleaning, since soap alone is active in this connection, uncombined oleic acid being inert.

This soap is liquid, and contains, in addition to soap, certain adjuncts which possess a specially powerful solvent influence on resin, asphaltum, tar, paint stains, cart grease, street mud, etc., so that the detergent effect is considerably heightened.

Weralin, which is made by O. Gans of Halle-on-Saale, is a yellow liquid, smelling, not unpleasantly, of oil of mirbane. When poured into a porcelain dish it soon evaporates, leaving a yellowish soapy residue. It is sold in condition ready for use, and forms a very useful detergent, and is not very much dearer than good benzine soap.

The liquid benzine soap, made by E. Koehler of Altenburg, is used for cleaning white and coloured glacé gloves. The benzine in this product easily removes all dirt and even the most persistent stains of perspiration by a single application with a piece of wash-leather, the treatment reviving the glove leather and improving the gloss and colour. A pint and a half will clean about forty pairs of gloves, the only after treatment required being a simple rinsing with benzine.

CHAPTER II.

EXTRACTIVE DETERGENTS AND DETERGENT MIXTURES.

A RECENT addition to the ranks of the extractive detergents: benzine, benzol, sulphuric ether, fusel oil (fermentation amyl alcohol), chloroform, alcohol, etc., is carbon tetrachloride. Before, however, going more closely into the properties of this latter, mention will be made of a few of the detergent mixtures that have been recommended of late. For instance, it has been proposed to replace ether for removing grease stains, and all those of a resinous or tacky nature, by mixtures of ether with benzol (or benzine), amyl acetate, methyl alcohol or ammonia. Mixtures of this kind have been put on the market under the name "Benzolinar". A typical composition of such mixtures is: benzol 4 parts, ether 1 part, and pure amyl acetate 1 part. Mixtures like the following: alcohol 3 parts, ether 3 parts, and ammonia 1 part, or equal parts of these three ingredients, have long been known. A useful recipe for preparing a mixture suitable for removing stains of all kinds is to dissolve 15 parts of soft soap, and 7½ parts each of calcined soda and borax in 910 parts of warm, distilled water, the cold solution being incorporated with a mixture of equal parts of ether, ammonia and methyl alcohol.

CHAPTER III.

CARBON TETRACHLORIDE.

PROPERTIES—Carbon tetrachloride, CCl_4 (tetrachloromethane, benzinoform), is a dense (sp. gr. 1·6), colourless, transparent and mobile liquid, with a neutral reaction. It is readily volatile, even at low temperatures, and has a peculiar smell, resembling that of chloroform. It boils at 77° C., but is absolutely uninflammable, and is incombustible in the condition of vapour, though it possesses the peculiar property of imparting a green tinge to a blue flame, and colours a green flame blue. If a strip of paper be dipped half-way into carbon tetrachloride and lighted the flame will go out before the middle of the strip has been reached.

Carbon tetrachloride is insoluble in water, and also in dilute alcohol below 75 per cent. strength by volume, and in glycerine. On the other hand it dissolves readily in acetone, glacial acetic acid, oleic acid, liquid carbolic acid and aqueous solutions of carbolic acid, as also in ethyl alcohol, methyl alcohol, amyl alcohol, chloroform, chloroform-alcohol, carbon disulphide, benzol, ether, ether-alcohol, oil of turpentine, petroleum and all petroleum distillates, ethereal and fatty oils and resin oils.

It dissolves oils, fats, wax, ceresin, spermaceti, paraffin wax, stearine, boiled oil, lacquers, shellac, asphaltum, pitch, resins, balsams, coal tar, pine tar, gutta-percha, caoutchouc, and hard and soft soaps.

Carbon tetrachloride is non-explosive; and another important quality in connection with its use as a detergent is the fact that it does not affect the colour of dyed fabrics.

Since, as mentioned above, tetrachloride rapidly and effectually dissolves all oils, fats, resins, paraffin, etc., it can be used to remove stains produced by those substances, and also such as are caused by butter, milk, gravy, lacquers, varnishes, oil paints (even old paint marks), tar, train oil and cart grease. It is equally efficient with chloroform as a solvent for oil paints, though a mixture of the two is better still, and will completely remove all trace of oil paint or tar from white materials. Unlike other detergents, no rings or annular markings are left when tetrachloride is used; and it is therefore specially adapted for cleansing light coloured articles. A mixture of equal parts of tetrachloride and acetic ether with 2 parts of rectified fusel oil is also used; and this mixture will take out the stain produced by red oil paints thoroughly and quickly.

The best means for getting rid of such stains is to moisten a clean rag, cotton wool or small sponge with tetrachloride, and keep on rubbing (or dabbing) the seat of the stain gently until the mark has disappeared. The cotton wool or rag should be frequently renewed, and thoroughly moistened with the tetrachloride.

If it be feared that even careful rubbing may injure the article (or the fibres composing it) a sheet of white filter paper is folded about four times, well moistened with tetrachloride, and laid under the stain, the latter being then covered with a similarly folded filter paper. On pressing the top paper firmly, preferably with a cold flat iron, the stain will be dissolved out and absorbed by the solvent. This treatment is repeated until no trace of the stain is left. To damp the stain with tetrachloride and then rub it dry with a rag is a wrong practice, since it merely causes the dissolved staining material to spread out and form a larger stain with a well defined rim.

Carbon tetrachloride was placed on the market at one time as a substitute for benzine. Although its chief advantages—

absence of fire and explosion risks—are universally admitted, it is still often stated that tetrachloride is inferior to benzine for hygienic reasons, on account of its anæsthetic properties, which are analogous to those of chloroform. The experiments of Professor Lehmann, however, have demonstrated that benzine possesses undoubted narcotic properties, and is decidedly more poisonous than carbon tetrachloride. In the laboratory of the Griesheim-Elektron Chemical Works, during experiments on the industrial application of carbon tetrachloride, large quantities of this solvent were evaporated (partly by design and partly by accident) and were inhaled by the chemists and their assistants, without any injurious effects, even when the vapours were breathed for several days in succession. On the whole it must be assumed that carbon tetrachloride is of no greater importance, in a toxicological sense, than benzine or chloroform, benzine being, moreover, narcotic in smaller quantities. The absence of fire and explosion risk is also an important advantage over benzine, from the standpoint of public safety. A number of makers put tetrachloride on the market under different names (benzinoform, antiflammin, etc.).

CHAPTER IV.

ACETO-OXALIC ACID AS A DETERGENT; SPECIAL METHODS OF REMOVING STAINS.

SEYDA'S aceto-oxalic acid, *i.e.*, oxalic acid saturated with 10 per cent. acetic acid, is worthy of mention among the newer detergents. Solutions of oxalic acid have long been in general use for removing rust stains from articles of clothing; but the work is performed more efficiently with aceto-oxalic acid. If the stain does not disappear at once an iron rod, dipped in the liquid, is applied to the spot and rubbed gently over the surface. Except in the case of very old stains complete eradication will be obtained.

Mention should also be made of the little known galvanic method, in which rust stains are removed from loose fabrics by boiling in weak sulphuric acid, in a copper pan into which is dipped a piece of zinc wrapped in linen (in order to protect the goods from the zinc flakes detached as the metal dissolves in the acid). A jacketed pan is preferably used. Even old rust stains can be quickly removed by this treatment.

In place of the ordinary method of removing ink stains by oxalic acid, followed by potassium permanganate, Seyda recommends the following:—

Oxalic acid is saturated with 10 per cent. acetic acid (see aceto-oxalic acid, above), and 1 part of the product is mixed with 4 parts of spirit of wine. The solution, which depends for its action on the solubility of iron oxalate in alcohol, will eradicate stains caused by ferrogallate inks; and it may also be used for stains arising from copying inks and aniline inks.

It must, however, be applied with care to coloured stripe goods, as there is some risk of the colours running, so that an aqueous solution of the mixed acids is preferable for such fabrics.

One of the chief advantages of the alcoholic solution is that it will dissolve ink stains on light coloured fabrics without affecting the dye; and it is also applicable for removing coloured stains, such as those produced by chlorophyll (grass stains).

Blood stains are soluble in warm water containing a little ammonia, and can be removed in this way. It has also been found that glacial acetic acid is useful for the same purpose, in the case of coloured fabrics, since it does not make the colours run.

Metallic oxide stains, which are usually brownish blue in appearance, are very difficult to remove from fabrics and have to be dealt with by a combined method. The stains are first dabbed with zinc chloride, and after the material has been passed over a steaming apparatus, potassium cyanide—which is highly poisonous and must therefore be handled with extreme care—is dabbed on at once. After washing with distilled water the stains are treated with a little formic acid, and well rinsed again. This treatment will entirely remove the marks.

CHAPTER V.

BLEACHING PROCESSES USED IN CHEMICAL CLEANING.

SHOULD the application of solvents (benzine, alcohol, carbon tetrachloride, etc.) fail to produce the desired effect, recourse must be had to bleaching.

Bleaching with Potassium Permanganate.—If a clean or dirty fabric (of cotton, wool or silk) be dabbed with a solution of potassium permanganate, the latter is at once reduced, and a brown stain of manganese hydroxide is formed. The reaction can be expressed by the equation:—

$$2KMnO_4 = Mn_2O_3 + K_2O + 2O_2,$$

the manganese oxide combining with water to form the hydroxide.

In the warm the reaction proceeds as follows:—

$$2KMnO_4 = 2MnO_2 + K_2O + O_3,$$

the manganese peroxide in this case forming the hydrated peroxide by combining with water.

Reducing Effect of Sulphur Dioxide.—If the brown stain be touched with a solution of sulphur dioxide (sulphurous acid) the bleaching action of the potassium permanganate is revealed. The powerful reducing agent, sulphur dioxide, deoxidises the brown manganese peroxide or hydroxide to manganous oxide or hydroxide, the sulphurous acid being itself oxidised to sulphuric acid. This acid combines with the manganous oxide to form manganous sulphate, a nearly colourless salt, which can be readily washed out of the fabric with water, leaving the site of the stain bleached to a pure white.

and thus demonstrating the bleaching action of permanganic acid.

If the amount of sulphurous acid used be too small it may happen that a brownish stain is left, a portion of the peroxide having remained intact. The excess of sulphurous acid used must be completely washed out, or it will be gradually oxidised to sulphuric acid on the fabric, the fibres being then corroded and rendered brittle. This may occur at once if the fabric be ironed.

Reduction with Hydrogen Peroxide.—More recently it has become the practice to replace sulphur dioxide, as a reducing agent for permanganate, by hydrogen peroxide, sodium peroxide, oxygenol or hydrosulphurous acid.

Hydrogen peroxide is immediately decomposed, on contact with manganese peroxide, into water and active oxygen ($H_2O_2 = H_2O + O$), so that an intensified bleaching effect is set up.

It may possibly happen that an insoluble layer of manganese peroxide is formed on the fabric, and prevents the complete decomposition of the excess of potassium permanganate on the fibre, in which event this permanganate also is reduced by contact with hydrogen peroxide, so that a further quantity of bleaching oxygen is subsequently brought into action on the stained portion of the cloth from two sources. In this after treatment the addition of acid to the hydrogen peroxide serves the purpose of converting the manganous oxide formed by reduction into a readily soluble salt that can be got rid of by washing.

For the above reasons sulphur dioxide is never used with hydrogen peroxide, because it would absorb a large proportion of the active oxygen from the peroxide for its own oxidation to sulphuric acid.

Formic acid and acetic acid, which have been proposed, also undergo partial oxidation in hydrogen peroxide solution, so that the mixture needs to be used in a fresh state. The action is, however, too slow.

Oxalic acid and phosphoric acid are also used in chemical cleaning; but form, with manganous oxide, salts that are only sparingly soluble in water (manganese oxalate and manganese phosphate), these being then very difficult to wash out of the fabric, even when very dilute solutions are used. Oxalic acid, indeed, should be discarded entirely, since, apart from the relative insolubility of the resulting salt, a portion of the acid is decomposed, with liberation of carbon dioxide, on contact with manganese peroxide, and its effect is thus lost. On the other hand, oxalic acid is capable of damaging the fabric to an equal extent with sulphuric acid.

Phosphoric acid is not attacked by hydrogen peroxide, and *vice versâ;* and it also remains quite unchanged in contact with manganese peroxide. Since, therefore, this acid retains its solvent power for manganous oxide, and the resulting acid phosphate is more readily soluble than the oxalate, the employment of phosphoric acid is indicated.

The above-mentioned after treatment of the brown stains of manganese peroxide on the fabric may be carried out with either pure hydrogen peroxide, or, in place of the latter, with the peroxide liberated by treating sodium peroxide or oxygenol with an acid.

Reduction with Hydrosulphurous Acid.—In all cases where sulphur dioxide is inapplicable, A. Seyda makes use of hydrosulphurous acid, which may be prepared, for instance, by shaking up 50 c.c. of sodium bisulphite solution (diluted with an equal volume of water) with enough zinc dust to cover the point of a knife. As soon as the reaction has terminated the mixture is diluted with water, shaken up, and filtered through cotton wool without delay. The filtrate is treated with 20-50 c.c. of acetic acid and 100 c.c. of boiling water, the product being then ready for use as a reducing agent. This reagent may also be replaced by the hyraldite described in Part I. It should be pointed out that hydrosulphurous acid rapidly decomposes in an aqueous solution.

Seyda's Reduction Process.—Seyda recommends the following for chemical cleaning without heat:–

1. Commercial hydrogen peroxide, mixed with an equal volume of 10 per cent. acetic acid, will readily dissolve manganese oxide, or potassium permanganate reduced on the fibre, without the application of heat.

2. A useful reducing agent can be prepared from sodium peroxide by the following means:—

A teaspoonful of sodium peroxide is dissolved in 100 c.c. of dilute sulphuric acid (1 part acid in 5 of water), enough additional peroxide being added to give an alkaline reaction, and the mixture treated with an equal volume of 10 per cent. acetic acid and a teaspoonful of ammonium chloride (sal ammoniac). The chemicals must be used in the order given.

3. To prepare the reducing agent from oxygenol, a teaspoonful each of oxygenol and ammonium chloride is placed in a glass holding about 200 c.c., whereupon 100 c.c. of water and 100 c.c. of 10 per cent. acetic acid are added. The solution clarifies quickly. The addition of ammonium chloride is to accelerate the solution of the manganese peroxide in the acetic acid.

The solution prepared from sodium peroxide is more sluggish in action than the oxygenol preparation, owing to the presence of saline constituents (sodium sulphate), which greatly retard the dissolving of the small quantities of manganese oxide or manganous oxide. This explains why the addition of ammonium chloride may be omitted when hydrogen peroxide is used. The solution mentioned above contains 5 per cent. of acetic acid, which strength cannot be exceeded without risk of injury to the colour of dyed materials. Formic acid may be used instead of acetic acid. By this method stains of all kinds can be removed from white, undyed or light coloured fabrics that have been dyed with rhodamine, alkali blue and chrysophenine. Unless great care be observed in the chemical cleaning of dyed fabrics a risk is easily incurred of the dye being bleached as well as the stain, so that the parts affected appear white. The only remedy, then, is to re-dye the bleached portion with a suitable dye. The behaviour of dyed goods in presence of hydrogen peroxide will be dealt with later, in connection with the employment of that substance as a detergent.

Permanganate bleaching is frequently employed in conjunction with other detergents. As already mentioned, the bleaching of stains is effected by dabbing with permanganate solution and redissolving the reduced manganese oxide.

Combined Method of Removing Stains.—Stains that are difficult to eradicate (such as those caused by scents) can be removed, from white fabrics especially, by the following combined method :—

The fatty substances are first extracted by means of a solvent (preferably carbon tetrachloride), and the site of the stain is then touched successively (without intermediate washings) with undiluted ammonia, oxygenol solution and oxalic acid solution. After the last treatment the place is thoroughly washed, dried, brushed over with alcohol (especially with silk goods), and then dried completely. Only very old stains will stand this treatment; and these may be removed by permanganate bleaching, followed by treatment with hydrogen peroxide, in conjunction with acetic acid or formic acid (see above). This method is often employed, though the fact that oxalic acid endangers the fabric constitutes an objection; and it has also been found that stains removed by means of oxalic acid and oxygenol exhibit a brown coloration again after a short exposure to light and air. For this reason oxalic acid may be preferably replaced by formic acid or acetic acid.

Hyraldite as a Detergent and Bleaching Agent.—This substance, the instability of which has now been remedied by the addition of weak acids, is suitable for removing coloured stains. For this purpose a small quantity of hyraldite is dissolved in about 100 c.c. of water, acidified with 15 drops of 10 per cent acetic acid and previously heated to boiling. If the stained fabric be folded to a point and dipped for a few seconds in the warm solution the spots of colour will disappear. This method can always be used for white fabrics, and also for such as have been dyed with rhodamine, alkali blue and chrysophenine; but if applied to other dyed fabrics (whether light or dark coloured) that have been stained, a preliminary trial should be made in some inconspicuous part of the fabric, to see how the dye is affected, if at all. In many cases it will be found possible, with a suitable solution of hyraldite, to remove the stains without affecting the dye.

Sometimes a yellow mark is left where a stain has been removed by hyraldite, but this can be eradicated by treatment with oxygenol solution (see later), the same being also the case with the yellow marks sometimes appearing when goods that have been freed from stains by permanganate are ironed, a warm solution of oxygenol being employed for this purpose.

Hyraldite is sometimes used as an adjunct in chemical cleaning. This preparation is obtained as a dry, crystalline mass when formaldehyde is allowed to react on the hydrosulphite of an alkali or alkaline earth. Stains, such as those of Bordeaux, that cannot be removed from clothing by means of the usual detergents, may be treated with hyraldite, which will bleach the majority of shades produced by artificial dye-stuffs without injury to the fabric, the material being re-dyed locally afterwards. The portions to be bleached are first treated for a short time with a hot, dilute solution of carbonate of soda or of ammonia, to remove as much of the dye as is soluble therein. After careful rinsing the rest of the dye is discharged by means of a liquid consisting (for light shades) of 3-5 per cent. of hyraldite A (previously dissolved in warm water) and 2-3 per cent. of acetic acid, the proportions being increased to 6-10 per cent. and 4-6 per cent. respectively for dark shades. As a rule, the amount of hyraldite required depends on the depth and resistant properties of the colour stains to be removed. The liquid must be used as hot as possible, and should therefore be heated to boiling in a separate vessel and maintained at that temperature. In most cases the stains can be discharged by repeated treatment. Previous to the final treatment, it is advisable to add a little acetic acid to the discharging liquid. Finally, the treated portions of the fabric are thoroughly rinsed, first with cold water and then with hot. Before applying the hyraldite treatment a preliminary experiment should be carefully made with hot alum solution, which often furnishes good results in the case of stains that are difficult of removal.

CHAPTER VI.

HYDROGEN PEROXIDE AS A DETERGENT.

THE properties of hydrogen peroxide have already been described in Part I.

To use commercial (10 per cent.) hydrogen peroxide as a detergent a bleaching liquor is prepared from the peroxide and water in equal volumes. The liquor is heated to near boiling, rendered alkaline with sodium silicate, and mixed with a little shredded white Marseilles soap. With this liquor the stained portions are dabbed until bleached, a plug of cotton wool, wound on a stick, being used for this purpose, on account of the bleaching action of hydrogen peroxide on the skin. The moisture must be taken up from time to time, or it will spread and bleach larger portions than desired.

In chemical cleaning, hydrogen peroxide is usually employed after permanganate; but there are many instances in which it can be used direct with advantage.

After the stains have been gone over with the peroxide solution the fabric should be exposed to light and air for several hours, with frequent dampings, then moistened several times with the peroxide again and placed in a warm room to dry.

If the stains are insufficiently bleached by this treatment they should be well brushed over with water and treated with dilute acetic acid, or, if necessary, with the aceto-oxalic acid already mentioned; after which the fabric is thoroughly scrubbed with water and finally dried.

A number of hydrogen peroxide preparations, of different strengths, are obtainable in commerce, among them being "perhydrol," containing 30 per cent. by weight of peroxide and forming a chemically pure, water-white solution, of sp. gr. 1·15 at 15° C. Since this perhydrol, when stored in Merck's original bottles, will keep for a long time, it is always possible to prepare a pure solution of hydrogen peroxide of any desired strength. All that is necessary is to see that the bottles—which should, preferably, be stored in a dark place—are properly reclosed after use, and that the ordinary temperature is not exceeded to any large extent.

To ascertain the behaviour of hydrogen peroxide during the removal of various stains, experiments were conducted with pure 3 per cent. commercial hydrogen peroxide solution, and with perhydrol solution, containing 1 part of perhydrol in 9 parts of distilled water. Similar results were obtained with the above-mentioned hydrogen peroxide solution mixed with sodium silicate and soap.

Stains caused by coffee, chocolate and cocoa can be removed by repeated dabbings and gentle rubbing.

In some cases (strong stains in particular) a few drops of the preparation must be allowed to act on the stain for a short time, the liquid being, in all cases, then taken up with cotton wool (see above). When pure hydrogen peroxide is used it is advisable to dab a little ammonia on the stains beforehand, or to add ammonia to the hydrogen peroxide. This latter mixture will also remove stains due to grass, beer, milk or fruit juices, the places being afterwards well dried with a white woollen rag, in order to prevent annular markings, especially on light coloured fabrics.

Red-wine stains can be cleared away, in many cases, with hydrogen peroxide solution without addition of ammonia, but the ammonia mixture is efficacious in the case of blood stains. It may also be used for ink stains, several applications being required, a previous careful dabbing with hydrochloric acid being necessary for iron inks only. Rust stains must be carefully touched several times with hydrochloric acid, the resulting (yellow) ferric chloride being taken up as completely as possible with cotton wool, and the remainder treated with hydrogen peroxide until the colour has entirely disappeared. Woollen and linen goods are afterwards washed with water, silk fabrics being rubbed in distilled water.

Mildew and yellow and brown stains, frequently appearing on white fabrics, may generally be removed with hydrogen peroxide, a preliminary careful dabbing with dilute hydrochloric acid being necessary in some cases.

Many stains produced by tar or cart grease can be eradicated by the hydrogen peroxide solution mentioned at the beginning of this chapter, or with a mixture of peroxide and ammonia, followed by rinsing with a warm solution of soap.

The bleaching solution mentioned at the head of the chapter may also be used for cleaning white gloves, an alternative method being as follows: white doeskin gloves, for instance, are first washed in lukewarm water containing Marseilles soap, and are then rinsed thoroughly in soft water. They are next entered and worked in a lathering solution of Marseilles soap containing 3 per cent. of hydrogen peroxide, drained, and left to dry slowly in a draught. The hydrogen peroxide bleaches the leather a fine white, and the residual soap restores pliability. When dry the gloves can be rendered more supple by energetic rubbing.

Since the ordinary commercial hydrogen peroxide (10-12 per cent. by volume) cannot remove obstinate stains, a stronger solution is sometimes used in chemical cleaning, especially for ink stains and the yellow or brown markings caused by perfumes.

Owing to the bleaching action of hydrogen peroxide on dyes it is largely used for eradicating stains on white fabrics; but long experience has shown that its application is by no means restricted to this class of material.

Behaviour of Hydrogen Peroxide toward Coloured Fabrics.—To test the action of hydrogen peroxide on coloured materials a large number of dyed fabrics (wool, shoddy, cotton, silk and half-silk) were treated for a short time with hydrogen peroxide or perhydrol solution (with and without ammonia), the conditions of the experiment being similar to those of chemical cleaning. In some instances the goods, stained with ink or rust, were carefully treated with hydrochloric acid and peroxide solution, in order to ascertain whether any alteration was suffered by the dye.

Of thirteen articles dyed with basic dye-stuffs, those coloured by means of safranine, rhodamine, new methylene grey, methylene green, indamine blue and malachite green were found to stand the treatment; none of them giving off their colouring matter when rubbed, or suffering any change in shade.

The same applies to articles dyed with resorcin dye-stuffs (eosine, erythrosine, etc.), although this group makes no claim to fastness.

Similar results were furnished by seven out of thirteen specimens dyed with acid dye-stuffs, *viz.*, acid violet, ketone blue, patent blue V, fast acid blue, violamine, fast acid violet and nigrosine.

Of ten specimens dyed with an equal number of nitro and azo dye-stuffs, such as azo yellow, Bordeaux, cloth red, fast brown, etc., only one, *viz.*, fast red, parted with its colour to some extent when rubbed after the treatment.

With the exception of alizarine brown and alizarine green the fourteen specimens dyed with mordanted dye-stuffs (alizarine blue, alizarine red, alizarine yellow, alizarine black, coerulein, acid alizarine green, etc.) stood the test.

Among the dyes for wool intended to stand milling, those prepared with anthracene yellow and chromium fluoride or potassium chromate were tested by allowing hydrogen peroxide solution (with ammonia) to act on portions stained with ink. The stains disappeared, without any loss or change of colour on the part of the fabric.

On dyeings carried out with milling yellow and anthracene acid brown (mordanted with potassium chromate), ink stains (iron ink) were removed by treatment with hydrochloric acid and hydrogen peroxide. The former shade was changed by the acid to brown, the other to black, but the original colours were restored by the action of the peroxide. Various stains were removed by the same reagents from dyeings obtained with milling red and wool red without any loss or change of colour on the part of the dyes; and a fabric dyed with alizarine blue (CS) also remained unchanged under the same treatment. Fabrics dyed with milling yellow, alizarine blue, fast diamine red (with potassium chromate), wool red, anthracite black, anthracene acid black and anthracene acid brown (with potassium chromate) also remained unaffected by hydrogen peroxide solution (with ammonia). Only about 23 per cent. of the fabrics examined parted with more or less colour when rubbed after treatment with hydrogen peroxide; and it may therefore be concluded that this detergent is also applicable to dyed fabrics, provided the necessary care be taken.

CHAPTER VII.

OXYGENOL AS A DETERGEN..

OXYGENOL is an inodorous, white powder, soluble in water and furnishing a decidedly alkaline solution that parts with its oxygen, the liberation of which is accelerated by dissolving the powder in water of a temperature of 95-105° F.

At this range of temperature the oxygen comes off in moderation, so that its bleaching action can be more satisfactorily utilised, whereas at 140° F. it escapes too rapidly, and is liberated completely at boiling heat.

Oxygenol forms a suitable reagent for discharging coloured stains from white articles, many of which stains can be removed by using an oxygenol solution warmed to 112-122° F. and applied repeatedly, a useful strength being about 1·2-1·5 per cent. Another solution, frequently employed, consists of 100 parts by weight of oxygenol, 100 parts of cold water and 20 parts of formic acid or 100 of acetic acid. This is restricted to careful dabbing of the stained portions at ordinary temperature, though it may also be applied after bleaching with permanganate.

Coloured stains that cannot be removed with hot oxygenol solution may be discharged with hyraldite, as already described, the operation being completed with a hot solution of oxygenol.

Fruit and coffee stains can be quickly removed by hot, concentrated oxygenol solution, but cocoa stains require to be repeatedly treated with the same reagent. Stains of red wine must be bleached with permanganate, followed by repeated applications of the hot solution of oxygenol.

Blood stains can be eradicated easily and quickly; but oxygenol is not so well adapted for the treatment of rust and ink stains, though good results are obtained in the case of singed marks and yellow stains and markings on cotton goods, lace, etc.

As already mentioned, oxygenol is specially used for removing stains on white articles. Owing to its bleaching action, however (like hydrogen peroxide), it is liable to discharge the colour of dyed fabrics.

Behaviour of Oxygenol toward Dyed Fabrics.—To investigate this behaviour, experiments were conducted with dyed woollen and cotton fabrics, the results showing that warm oxygenol solution has, in general, a more powerful bleaching effect than ordinary commercial hydrogen peroxide solution. The only aniline dye-stuffs, on cotton, that proved fairly resistant to lukewarm oxygenol solution were: new grey, indophenine, Bismarck brown, new fast blue and new fast grey. Of the dyes fast to milling, on woollen fabrics, only alizarine blue, diamine scarlet, wool red, anthracene acid brown (with potassium chromate), anthracite black (various marks) and anthracene acid black were able to stand the action of oxygenol solution, warmed to 113° F., and giving off oxygen freely. Milling yellow and milling red were also fairly resistant, and only parted with a little colour when rubbed, whilst anthracene yellow and milling yellow (O) withstood rubbing.

Hence oxygenol can be used with success in many instances, particularly for removing stains from white articles.

CHAPTER VIII.

SODIUM PEROXIDE AS A DETERGENT.

SODIUM peroxide can be used in place of hydrogen peroxide as a detergent, the bleaching liquor being prepared in the following manner:—

Twenty parts by weight of formic acid, or 100 parts of acetic acid, are poured into 1,000 parts of water, 120 parts of sodium peroxide being then added in small portions and incorporated by continued stirring. The solution should be left to stand for an hour before use. It is applied either direct or after permanganate. For silk fabrics in particular the following is a useful alternative recipe:—

Ten parts of magnesium sulphate are dissolved in 1,000 parts of soft water, 3½ parts of sodium peroxide being added slowly and stirred in, followed by 3 parts of sulphuric acid. The reaction of the liquor is next carefully tested with litmus paper, and if found too acid is neutralised with a little sodium peroxide, acid being added if the liquor be alkaline. A stronger solution may also be prepared. The stains are dabbed with the hot liquor.

Sodium peroxide is also used for laundry purposes, either by adding it to the washing liquid in the machine, in a quantity appropriate to the materials under treatment, or else the articles, after having been washed for some considerable time, are entered into a hot bleaching liquor of sodium peroxide. This treatment makes the articles perfectly white; but the peroxide solution must not be too strong, or the fibres will suffer injury.

Except obstinate dye stains, nearly all stains usually caused on linen can be completely removed by the use of sodium peroxide in washing. Owing to its higher percentage of active oxygen this peroxide is more energetic than oxygenol. Dye stains are preferably removed with hot hyraldite solution before bleaching.

Sodium Peroxide Soap.—Beltzer recently made public a method of preparing soap containing sodium peroxide, the production of which is based on the property of the peroxide for forming a stable dry mixture with anhydrides. The soap is made from acid castor oil, colophony, sodium carbonate and sodium silicate. The strongly alkaline soap powder is then dried completely and thoroughly mixed with dry sodium carbonate and sodium peroxide in a rotary mixer, the mass being made into blocks in a hydraulic press. This soap is intended for textile purposes, such as bleaching raw cotton, raw flax, jute, ramie, pelts and fur. An alkali peroxide cartridge has been patented by M. Heise, Berlin.

CHAPTER IX.

SUNDRY NEW DETERGENTS AND CLEANSING AGENTS.

TETRAPOL.—This patented preparation is an oily yellow liquid, with a peculiar smell, like that of radishes. It is miscible with water in all proportions, and is a very efficacious agent for cleaning and scouring woollen yarns and other materials contaminated with grease. It has an alkaline reaction, and behaves like a soapy lye when mixed with water. It can only be used in chemical wet cleaning and as a detergent, but not in chemical dry cleaning.

Tetrapol is neither inflammable nor combustible. It is used only in the cold, or at temperatures below 122° F., and either of full strength or diluted with 2-8 parts of distilled or soft water. Grease stains may be removed by the application of a 25-50 per cent. solution, left in contact with the stain for an hour without rubbing, the stained parts being then wetted and rubbed between the fingers, after which the detergent is scrubbed off and the fabric brushed with soft water.

Oil and fat stains, especially from mineral oil, may be rubbed with tetrapol, treated with a little lukewarm soft water until a good lather is obtained, and then rinsed till all the tetrapol has been washed off, carrying with it the grease, dirt, etc.

The same treatment may also be used for removing blood stains, though a simple application of dilute tetrapol (1 : 4) will generally suffice. If the stains are not eradicated the first time, the treatment can be repeated, since no injury is done to the fabric or the dye.

In laundry work tetrapol is used like ordinary soap, and offers the advantage of not producing any insoluble lime compounds, so that it is easily washed out of the fabric. It does not impart any smell to the clothes.

Lavado.—This name is given to a preparation that may be used for laundry work and as a detergent. It is a syrupy, dark yellow liquid, smelling slightly of ammonia and turpentine, and forming a white alkaline emulsion with warm or cold water even when present in only very small quantity therein. It is composed of oil of turpentine, turpentine and ammonia; and is used in laundry work as an adjunct to the soaking water for white articles, its power of penetrating the fibres assisting in the elimination of dirt. For washing curtains König recommends two spoonfuls of lavado to each pail of water (at a temperature of 104° F.), the curtains being soaked in this solution for four to six hours, by the end of which time they are clean and may be rinsed out. Men's clothing may be soaked for half an hour in water (at 85° F.) containing three spoonfuls of lavado per pail. This will dissolve out all hard dirt and stains; and light coloured articles may then be finished by washing with soap, dark fabrics with washing soda and lavado. Woollen coverlets, which are often the habitat of disease germs, should be soaked in the same way as men's clothing, but for a longer period—several hours. This not only kills all germs, but facilitates the washing. The first washing bath should contain soap but no soda or ammonia.

If a second water is required to make the coverlets quite clean they need not be sulphured, but may be put through a good warm souring bath (sulphuric acid) and well rinsed afterwards. König considers that lavado is very useful for washing knitted goods, owing to the penetrative and detergent properties of the turpentine. It may also be found advantageous in the milling of cloth, for which purpose use is already made of two of its constituent ingredients: turpentine and ammonia. Another preparation (Lavado F) is oil of turpentine rendered soluble in water. It is a pale yellow, syrupy liquid, which turns milky when mixed with cold or warm water, and forms a good detergent.

Novol.—Novol B is a pale honey-coloured, oily, alkaline liquid, smelling rather like benzol. It mixes to a milky liquid with water and acts as a detergent on grease. This preparation is similar to Lavado F and tetrapol, all of them containing about 25 per cent. of a fat solvent and 25 per cent. of fatty acid.

In the laundry novol is added to the washing water after the latter has been softened with carbonate of soda; and it may also be added to the soaking water, for which purpose (with a little soda) it is better than soap. Articles washed with this preparation are beautifully white; the fibre is uninjured and retains its natural flexibility.

Weiss's Benzine Washing Preparation.—E. Weiss (French Patent 366,547) makes a preparation for cleaning textile fabrics by mixing 4 parts (vol.) of olein with 4 parts of ammonia (sp. gr. 0·910) and 1 of alcohol, the whole being heated to boiling and used in conjunction with benzine. Solutions of fat saponified with caustic alkali and the above quantity of ammonia may also be used.

Hexol.—This is a volatile yellow liquid, with a peculiar, but not disagreeable smell, and forms a concentrated detergent, which may be used as such, or diluted with about 2 volumes of benzine or 95-96 per cent. alcohol or a mixture of both. Shaken up with 5 parts of water, it gives a milky liquid, suitable for removing stains on white articles and the like.

In chemical cleaning it may replace fusel oil, chloroform, acetic ether, etc., and its application is followed by treatment with benzine, to eliminate all final traces of stain. It readily takes out stains arising from pitch, oil, tar, etc., and in the concentrated form is useful in removing old or obstinate stains caused by paint or tar. The dilute form (1 : 5) is better for washable materials that do not lose their shape (stiffening) when wetted, the stains being brushed over with this solution.

Sternberg's Detergent Oil is a yellow, inodorous, oily preparation, dissolving in water to a milky but clear solution, and is suitable for replacing tetrapol in washing coloured fabrics, since it prevents the "bleeding" of the dye, and imparts a soft texture to cotton and woollen goods. For white articles it is used in conjunction with washing soda, as a substitute for soap and soap powder.

Ozonite, also one of Sternberg's preparations, is a white, inodorous powder free from acid and chlorine. It is soluble in water, with effervescence, an alkaline solution being formed. In testing its detergent and bleaching properties it was found that a warm concentrated solution attacks such basic dye-stuffs as fuchsine (on cotton) and rhodamine (on wool); methyl violet (on cotton) and methylene green (on wool) being more strongly affected, and malachite green still more powerfully. Erythrosine (resorcine dyes) was also fugitive. Among the acid dye-stuffs the following were considerably affected: acid violet, opal blue and acid green (all on wool). A good deal of colour was also discharged from azo-yellow and fast-brown dyeings, though woollens dyed with azo-acid black and chrome brown suffered no injury. The mordanted dyes, alizarine yellow, alizarine orange, alizarine blue, alizarine brown, acid alizarine green, were able to stand warm concentrated ozonite, though alizarine red (RX, paste) on silk was strongly affected. It is therefore considered that ozonite may be used, in many instances, for removing colour stains from white fabrics.

It is also suitable for eradicating stains caused by fruit, red wine, cocoa, blood, etc., on white fabrics; but special care must be taken when applying it to dyed materials, especially those containing basic acid or resorcin dye-stuffs. A little ammonium chloride and acetic acid may be added to the concentrated ozonite liquor.

For laundry work ozonite may be used to the extent of two to four spoonfuls per 100 lb. of clothes, the solution being added to the final washing water in the machine. If lye be used the ozonite is added to it, care being taken not to bring the liquor up to the boil too quickly, or the oxygen will be expelled prematurely and its bleaching action lost.

The temperature should be raised slowly so that the liquor remains at between 105° and 122° F. for twenty or thirty minutes, and only heated to boiling at the last. Since ozonite does not give off any smell the articles washed with it do not need any special rinsing.

Ozonal is a new laundry preparation sold in cubes or tablets. According to A. Beythien it consists of 9 parts of petroleum and 1 of resin and soap. In comparison with liquid petroleum—so well known as a detergent for grease—it has the advantage of not floating on the top of the water, but of forming a homogeneous washing liquor therewith.

Quillola is a soap powder, intended as a complete substitute for quillaya rind. Care should be taken not to inhale the powder while adding it to the water in making the solution, as it causes violent and prolonged sneezing. It is specially adapted for cleansing dyed silks.

Gruner's Washing Powder.—This is a yellowish, greasy powder containing about 80 per cent. of pure soap and 9 per cent. of sodium peroxide. This latter is decomposed by water to form free caustic soda and oxygen ($2Na_2O_2 + 2H_2O = 4NaOH + O_2$), though as a matter of fact only about two-thirds of the peroxide comes into action. The powder has a powerful bleaching effect and is a good cleansing agent. No scrubbing of the clothes is required.

Eureka Washing Powder contains about 48·15 per cent. of fatty acids and is free from deleterious ingredients. For use it is dissolved in hot water, the solution being then diluted with 6-8 volumes of cold water. It cleanses woollen and linen goods, making them as white as new, without injury to any dye-stuffs they may contain.

Detergent Soaps that Liberate Oxygen.—Up to the present no soap has been invented that is at once harmless and effectual as a cleansing, bleaching and antiseptic agent. According to Giessler and Bauer an efficient soap is prepared by incorporating with an ordinary stock soap an alkali perborate or percarbonate, either as a powder or mixed with fatty matters (lanolin, vaseline, paraffin, etc.) free from glycerine. About 10-20 per cent. of sodium or ammonium perborate or percarbonate is used, both classes of salt being thoroughly stable and rich in oxygen. These salts are not decomposed in soaps containing even as much as 20 per cent. of water. Even in water at over 104° F. the oxygen comes off slowly and steadily. The soaps containing these salts will readily discharge stains caused by red wine, bilberries, cocoa, etc., on white articles. The alkali persulphates have recently been employed for the production of bleaching soaps and soap powders, 5-10 per cent. and even more being added to solid soaps, a certain amount of sodium carbonate being also used to combine with the free acid that is always formed. For instance, 100 parts of sodium persulphate split up into 6·77 parts of oxygen and 41·52 parts of sulphuric acid, for the neutralisation of which 44·9 parts of calcined soda are necessary.

Klein's Detergent Soap.—This soap, which is applicable to stains of all kinds, especially on silk, calico, etc., and does not affect dyes, is made as follows: 2¼ lb. of Marseilles soap and 18 oz. of cocoanut-oil soap are shredded thinly and mixed with 4 oz. of alum, 1 oz. of alcohol, 9 oz. of potassium carbonate solution and 4 oz. of ox-gall, the whole being warmed. On the following day, ½ gall. of alcohol, four fresh eggs and 2 oz. of spirit of camphor are added, and the whole is stirred together energetically until intimately mixed.

Detergents for Sensitive Colours.—Dirty fabrics in sensitive colours may be cleaned with the following mixture: 10 parts of quillaya extract, 10 parts of borax, 30 parts of ox-gall and an equal quantity of Marseilles soap. For many purposes a cheaper mixture will suffice, *viz.:* 30 parts of strong ammonia, 40 parts of olein and 500 parts of water. On the other hand, there are cases where egg yolk (or Klein's preparation, see above) alone is admissible. In general, when sensitive colours are in question, it is advisable to make a preliminary trial with a lukewarm solution of perfectly neutral soap.

Paltzow's Detergent Soap.—This preparation is an excellent agent for removing stains of all kinds from even the finest materials and in the most sensitive colours, without injury to either the dye or the fibre. It is made of the purest fat, and contains the active ingredients of quillaya bark in a pure and concentrated condition. Despite its dark colour the preparation can be successfully applied to cleaning white woollen articles and the like. The stained parts being moistened with water, the soap is well rubbed in, the resulting lather being afterwards washed off with a little lukewarm water. The stains should never be brought into direct contact with the solution. The quillaya bark used in making this soap contains saponin, which acts like a perfectly neutral alkali soap, and is also used in making a number of textile and other special soaps.

In cleansing effect 500 parts of quillaya bark are equal to 1,000 parts of good soap, that is to say the former is twice as effective as the latter.

Wolzendorff's Achinin Soap.—According to the maker's statement, this white soap, which smells strongly of ammonia and oil of turpentine, contains active ozone and other bleaching, cleansing and detergent bodies, such as oil of turpentine, sal ammoniac, benzine and sodium silicate. It is suitable for removing stains caused by perspiration, oil, blood and tar on household linen.

Liquid Detergent Soaps.—A liquid detergent soap may be prepared by shredding good white curd soap and dissolving it by shaking in ammonia, the solution being diluted with strong ammonia to the consistence of syrup. The mass is smeared over the stains and then washed off with lukewarm water.

Another preparation of this class is compounded from soft soap 1 oz., calcined soda ½ oz., borax ½ oz., ammonia (sp. gr. 0·910), ether and methyl alcohol 2 fluid oz. each, and distilled water 3 pints.

An ammonia soap for removing grease stains, etc., is prepared from 100 parts, by volume, of oleic acid, 50 parts of ether, 50 parts of chloroform, 500 parts of benzine and 100 c.c. of alcoholic ammonia, mixed together in the above order, by shaking. If a white emulsion be preferred the alcohol is replaced by twice its volume of pure water.

Potassium Cyanide and Photographer's Ink.—Brown and black stains on household linen (caused by hair dyes, medicines, marking inks) can be removed with a solution of potassium cyanide in lukewarm distilled water. Owing to the poisonous nature of the cyanide it must be used with the greatest care.

Silver nitrate stains can be removed by a mixture of sal ammoniac and corrosive sublimate (10 parts of each in 80 parts of distilled water). Another useful mixture is made from 300 parts of Glauber salt, 140 parts of bleaching powder and 280 parts of water.

Photographer's ink is made by mixing 1,000 parts of soap powder (from good curd soap), or an equal quantity of carefully made soft soap, with 100-200 parts of potassium cyanide, in the cold. This preparation will remove all silver stains caused by silver nitrate, marking ink, hair dyes, etc., in a very short time.

Detergent Liquids.—The following recipes are of recent introduction:—

(*a*) Thirty parts of olive-oil soap are dissolved, by shaking, in a mixture of glycerine 30 parts, strong ammonia 7 parts, ether 30 parts and water 500 parts.

To use this excellent preparation the stained portion of the article to be cleaned is laid over a cloth, and the liquid is applied to the stain with a sponge, rubbed gently over the surface for a few seconds, the solution being finally washed away with clean water.

(*b*) Alcoholic soap solution 100 parts, ammonia (10 per cent.) 50 parts, acetic ether 15 parts. This mixture is suitable for grease stains, which are moistened with the liquid and wiped with a woollen rag.

(*c*) Benzine 200 parts, ether 40 parts, acetic ether 30 parts and oil of turpentine 60 parts.

(*d*) Saponin 10 parts, dissolved in distilled water 500 parts, the solution being mixed with 20 parts of ammonia (sp. gr. 0·960). A useful preparation for cleaning off grease and dust stains.

(*e*) Carbon tetrachloride 650 parts, acetic ether 100 parts, alcohol 100 parts, alkali soap (soluble in benzine) 8 parts, benzine 142 parts.

This last preparation will not injure the material or the dye, acts easily and quickly, gives off no smell, is non-inflammable and incombustible, and evaporates without a trace. It will clean most stains, *e.g.*, those caused by sauces, grease, petroleum, varnish, tar, wax, oil paints, etc. The stains (on wool, silk, cotton, lace, carpets, felt, furs, etc.) are moistened with the detergent, lightly brushed, and finally dried with a clean cotton cloth.

Hummel's Detergent Liquid.—This is a French patent preparation, which is intended to obviate the fire risk and disagreeable smell resulting from the use of benzine. With regard to its composition, A. Colin reported that the addition of 1 part of alchol to 3 parts of benzine increases the solvent power of the latter considerably, whilst the addition of carbon tetrachloride facilitates the solution of tar, fats, greases, paraffin, stearine and the like as well as lessening the fire risk and entirely eliminating the smell of benzine during its own complete evaporation. Acetic ether is a special solvent for resins and varnishes, so that the mixture composed of these various cleansing agents presents decided advantages over benzine used alone.

Detergent Paste.—A useful paste is obtained by mixing 2 parts of borax with 3 parts of ox-gall, and then carefully adding 20 parts of finely powdered tallow soap, followed by 1 part of oleic acid.

Another paste—sold in Germany as Kaiser-Flecken-Pasta—is a solid, yellow-white, soapy mass, which yields a saline efflorescence on long storage. It is designed for removing stains of various kinds, to which it is applied by rubbing, and is then rinsed off with lukewarm soap and water.

In using this paste as a detergent care is necessary when coloured articles are in question, especially when the paste is old. It is best adapted for white, dark brown, black or brown fabrics; and it may also be applied to woollen goods dyed with chrome and alizarine dye-stuffs.

Blanchissine.—This cleansing medium has been introduced by Boettiger (Lille) in two qualities.

Blanchissine No. 1 is made of: Caustic soda 8 parts, alcohol 20 parts, olein 24 parts, glycerine or vaseline 2 parts, oil of turpentine 4 parts and ultramarine 2 parts. One oz. should be added to every 10 galls. of water, and it is suitable for washing fine silks as well as ordinary household linen.

Blanchissine No. 2 is made of: Ammonia 64 parts, olein (glycerine, castor oil or vaseline) 5 parts, oil of turpentine 25 parts and benzine 6 parts. About 2 oz. are used to every 10 galls. of water, the materials (very fine goods, lace, etc.) being washed in a machine.

Henkel's Persil.—This laundry preparation contains: Water 31·9 per cent., sodium carbonate 25·4 per cent., sodium silicate 13·6 per cent., soap 20·1 per cent., hydrogen peroxide 6·3 per cent. and residual matter 2·7 per cent. The hydrogen peroxide is disengaged in consequence of an addition of sodium perborate.

Other recent cleansing agents are:—

Reinol, Triol, Tetra-Isol (soluble carbon tetrachloride), Benzin-Isol (soluble benzine), Terpin-Isol (soluble turpentine), Isobenzine soap (neutral benzine soap) and Iso soap, a new sulphoderivative of castor oil. This last soap is solid and resembles curd soap. It is characterised by a high percentage of fat, with a perfectly neutral reaction; it is free from Glauber salt and non-hygroscopic, though it does not dry hard when stored. It dissolves to a clear solution in water, remaining clear even in the cold. A 2-3 per cent. solution will stand an equal addition of any organic acid, such as formic acid or acetic acid, and does not form any lime soaps even with the hardest water; in fact it redissolves any ready-formed lime soaps present. Moreover, it will stand the addition of a certain amount of dissolved salts, like magnesium sulphate or magnesium chloride. Added to bowking liquor it reduces the time required for bowking by about one-half, whether in an open or closed kier, and with loose material, yarn or piece goods. The above preparation is put on the market by L. Blumer, Zwickau.

It is well known that certain fatty matters, softening adjuncts and mineral oils are very difficult to eliminate from woollen fabrics; and for this purpose Iso soap is very useful, owing to its double capacity of forming an emulsion with other oils, fats and mineral oils, and of not combining with lime to form insoluble hard soaps. As an adjunct to the usual soap baths it acts as a cleansing agent which imparts mildness of texture to the wool during scouring and milling.

According to H. C. Bradford, the following preparation is useful for cleaning carpets, as a detergent, and also for cleaning kitchen utensils, in addition to which it possesses the advantage of being uninflammable and readily saleable: Soap solution 120 c.c., 10 per cent. ammonia 60 c.c., gasoline 120 c.c., chloroform 20 c.c., potassium nitrate 10 grms., oil of wintergreen 10 c.c., and distilled water 1,000 c.c.

The potassium nitrate is dissolved in a little water. The ammonia is added to the soap solution, the chloroform, wintergreen oil and gasoline being run in in succession; and the two liquids are mixed by agitation, and made up to 1 litre with water. The wintergreen oil is used for its scent, and may be replaced by any other perfume desired.

The soap solution is prepared from: Olive oil 60 c.c., caustic potash 12 grms., and sufficient alcohol and water, in equal portions, to make the total volume up to 1,000 c.c.

The oil is placed in a dish, and to it are added 30 c.c. of alcohol and the potash dissolved in 30 c.c. of water, the whole being heated on the water bath until the oil is completely saponified. This result is accomplished when a sample is ound to dissolve to a clear solution in water. After cooling the mass, 500 c.c. of alcohol are added, with enough water to make 1 litre. The addition of 45 grms. of camphor and 15 c.c. of oil of lavender will give an excellent liniment.

A useful apparatus for removing stains has been introduced by Schwarzkopf, of Berlin, consisting of several layers of absorbent material, in the centre of which are embedded a number of rods of a soluble detergent preparation, arranged in such a manner that the edges of the rods and envelope together constitute a rubbing surface. The whole is surrounded by a metal sheath. On dipping the rubbing surface in a solvent liquid (water, alcohol, ether, etc.) the latter is absorbed by the material, so that the embedded preparation is partly dissolved, and is transferred to the seat of the stain by the act of rubbing.

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